SURFACE RADIOCHEMISTRY

THESIS

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CONTENTS

ABSTRACT

This thesis describes carbon - 14 tracer investigations of the ethylene hydrogenation reaction on supported metal catalysts.

The metals used in this study were nickel, rhodium, palladium, iridium and platinum, as 5% preparations on alumina supports. Reduction of the catalysts by hydrogen was carried out 'in situ' for six hours at 500°C. This was followed by a six hour period of degassing at the same temperature.

Quantities of ethylene - C - 14 were then admitted to the catalyst at 20°C until saturation of the surface was observed by an end-window G - M tube placed within the catalyst vessel. This G - M tube was then used to observe the fate of the pre-adsorbed ethylene - C - 14 when an equimolar mixture of non-radioactive ethylene and hydrogen was admitted to the catalyst vessel. Under these conditions ethylene hydrogenation was observed to take place. The effect of non-radioactive ethylene on the pre-adsorbed ethylene - C - 14 was also studied.

It was observed in all cases that only part of the pre-adsorbed ethylene was removed by hydrogenation, and molecular exchange with ordinary ethylene. The retained material could not be r emoved by pumping or by treatment with pure hydrogen.

The results are presented in the form of percentage of the initial radioactivity retained on the surface, and this quantity was found to vary from one catalyst to another in the sequence:

Pd	Ni	Rh	Ir	Pt
65%	22.5%	22.5%	14%	7%

In the case of nickel, pre-treatment with hydrogen had no noticeable effect on subsequent ethylene - C - 14 adsorption or retention. Ethylene - C - 14 adsorbed on a nickel-alumina catalyst was noted to be reversibly adsorbed to some extent and it could be removed by evacuation of the catalyst vessel. It was further observed for palladium that catalysts poisoned by oxygen, which were inactive for ethylene hydrogenation, were yet capable of adsorbing ethylene - C - 14.

Attempts to decide on the nature of the adsorbed species were then undertaken. Correlations were sought between retention and heat of adsorption and also with the ability of the metals to break carbon-hydrogen bonds as indicated, for example, by deuterium exchange. On the other hand the possibility that the retained species are associatively adsorbed was considered with regard to the tendency of the metals to promote alkyl reversal.

No clear cut decision is possible on this question for with the exception of palladium apparent correlations exist for both models. A correlation was also sought with σ-π-complexing ability.

Finally an attempt to explain the apparent correlation between retention and selectivity for acetylene hydrogenation is described.

The results have significance in the interpretation of the absolute rates of catalysed reactions in that, for the first time, the fractions of each surface active in hydrogenation have now been measured.

CHAPTER 1

INTRODUCTION

In heterogeneous catalysis the rates of thermodynamically feasible reactions are increased by interaction of the reactant species with a solid surface which is usually that of a transition metal. The reactant may be in solution or in the gas phase. Gas phase catalysis presents a simpler system for fundamental studies since solvent effects need not be considered.

One of the principle aims of catalyst studies is to understand reaction mechanism in terms of the physical and chemical properties of the metals involved.

Two types of interaction between gas and surface have been noted. The former requires an activation energy and tends to occur at higher temperatures than the latter which depends only on physical forces of the type involved in liquifaction. The same gas may therefore show both forms of adsorption on a metal surface, the amount adsorbed showing a minimum at the temperature corresponding to the transition from one type to the other.

By mechanism, is meant, all the individual events taking place simultaneously or consecutively in producing the overall reaction. Only the activated complex need be adsorbed on the surface for the reaction to be classed heterogeneous. Adsorption of reactants or products is not necessary. However, although this possibility

exists it has never been observed in practice. All reactions so far studied fall into two schemes. In some cases, probably the majority, the Langmuir-Hinshelwood [1] mechanism is held to be operative in which both reactants are chemisorbed. In the Rideal [2] mechanism on the other hand, only one reactant is chemisorbed, the other reacting from the gaseous or physically adsorbed state.

Thus a study of chemisorption is necessary if the phenomenon of catalysis is to be understood. Work on chemisorption has been concerned with equilibria and rates. The amounts of gas adsorbed at equilibria depend on the nature of the adsorbate, the temperature and the pressure. Another type of investigation involves measurement of heats of adsorption. This may be done by direct calorimetry, or by use of the Clausius-Clapeyron equation if equilibrium pressures corresponding to fractions of the total surface covered are measured. Kinetics studies consist of measuring the rates of adsorption and desorption. Activation energies may be determined from these measurements by making use of the Arrhenius relationship. Various models [3] have been postulated for the adsorption process involving, for example, one or two point adsorption. Adsorption isotherms are calculated on this basis and compared with the data of experiment. In this way information on the adsorption process has been built up for a large number of reaction systems.

Attempts are then made to relate this information to the kinetic laws of surface reactions. In particular, reaction rates

may be calculated using Absolute Reaction Rate Theory [4] and mechanistic models based on the above experimental results. In these calculations the surface of the catalyst might be taken to be such that on the surface are exposed 10^{15} atoms per cm^2. If the calculated rate is too high it is probable that the surface exposure of chemisorption sites is less than this. If too low, it is probable that the transition complex possesses rotational or translational energy. Thus the theory may be used to throw light on these mechanistic points.

Surface area is an important parameter in the study of catalyst surfaces. Catalytically active metals are studied in various physical states. [5] They may be studied as evaporated films, as powders, wires or single crystals. Or again they may be studied as supported catalysts where the metal is dispersed over comparatively inert support material such as alumina or silica. Clearly it is impossible to correlate results from experiments on one metal with those on another preparation of the same metal if the surface area being dealt with is not known in both cases. Moreover the catalytic activity of one metal and that of another cannot be compared without a knowledge of the areas involved.

Accordingly much work has been done on the estimation of surface areas. [6] In the early days the extent of chemisorption was taken as a measure of surface area. However there was some

doubt as to whether chemisorption took place over the whole surface or only part of it. Gradually physical adsorption superseded chemisorption in these studies.

Examination of some isotherms indicated a point which might be taken to represent the completion of a monolayer. Furthermore gases of approximately the same molecular dimensions were adsorbed to approximately the same extent before the isotherms showed this point, known as the 'point B'. The volume of gas adsorbed at this point and a knowledge of the molecular area enabled the surface area to be estimated. Later, B.E.T. theory[7] enabled isotherms not showing the 'point B' to be used in the estimation of surface area thus generalising the procedure.

The area so estimated may be expressed as the number of adsorption sites per cm^2 in contact with the ambient gas. This sort of area measurement is valuable in ascertaining the extent to which different methods of catalyst preparation affect the total surface area. It is also useful in correlating data obtained from different experiments on the one metal.

However chemisorption rather than physical adsorption is the important step in catalysis. Thus unless the surface is energetically homogeneous so that chemisorption can take place on all the available sites, the active area of the surface is still unknown. Therefore the problem of relating catalytic

activity to the physical and chemical properties of the metals is still unsolved, unless it can be shown that surfaces are energetically homogeneous.

Since bonds are to be formed between the adsorbate and the surface the degree of unsaturation of the surface atoms will be important. This will vary depending on whether the atom is in or at the boundary of a crystal face. Again, the degree of unsaturation of atoms associated with crystal defects may be expected to be different from that of other atoms. Taylor[8] was the first to suggest that surfaces would in fact be heterogeneous and that only a fraction of the total available sites would be catalytically active. This gave rise to the concept of 'active areas' for which experimental support was obtained by Pease and Stewart[9] who showed that catalytic activity was considerably more susceptible to poisoning than was adsorption.

Later it was observed by Beek[10] that heat of adsorption varied with degree of surface coverage. He explained these results by supposing that certain sites adsorbed gases more readily than others. However other explanations are possible. As suggested by Trapnell,[11] the observed fall in heat of adsorption could be due to increased dipole-dipole interactions in the ever increasing adsorbed phase. De Boer[12] on the other hand

suggested a gradual change in work function as adsorption proceeds, as the explanation. Thus Beek's results are not sufficient to preclude a homogeneous surface.

No matter what processes are operative during adsorption, once a monolayer is formed all the adsorbed molecules will be in the same environment if the surface is homogeneous. No adsorbed species will therefore desorb in preference to another. If on the other hand the surface is heterogeneous preferential desorption is to be expected. This should arise because the gas admitted to the surface initially will adsorb on the most active sites available and consequently will be less easily desorbed than gas adsorbed subsequently. Thus if a quantity of labelled gas is adsorbed, followed by a non-labelled sample to complete the monolayer it should be possible to observe desorption of this latter sample first. Roginskii and Keier[13] using a differential isotope method were able to show that the isotopic distribution of the gas adsorbed first was the same as that desorbed last. The system studied was hydrogen-deuterium exchange on charcoal. They concluded that the surface was heterogeneous.

Kummer and Emmett[14] applied this method to the study of chemisorption of carbon monoxide on a promoted iron synthetic

ammonia catalyst. The results again suggested heterogeneity. However they noticed also a rapid partial exchange between adsorbed species. On applying the Roginskii/Keier method to reduced nickel on silica catalysts, Schuit [15] obtained an equilibrium mixture of hydrogen and deuterium as the desorbing gas. This suggests homogeneity of the surface.

However although the Roginskii/Keier method can demonstrate heterogeneity it cannot so demonstrate homogeneity. A result which suggests homogeneity can be explained in terms of surface mobility of adsorbed species on a heterogeneous surface. Nor can the possibility of surface mobility be excluded since elevated temperature treatment was employed to effect desorption.

In view of this Cranstoun and Thomson [16] adopted displacement by mercury as the means of desorption and were able to demonstrate surface heterogeneity in evaporated nickel films at 25°C.

Thus it may be stated that the differential isotope method has revealed surface heterogeneity wherever it has been applied except in those cases where surface mobility of adsorbed species cannot be discounted as a possibility.

Rhodin [17] using a micro-balance and single metal crystals has been able to observe varying rates of adsorption with different crystal faces. The matter was taken further by Gwathmey [18] who observed varying rates of ethylene hydrogenation on different

faces of large single crystals of nickel. These results give a clear indication that the observed heterogeneity of catalyst surfaces resides in the different properties of different crystal faces and gives support to the Geometric Factor Concept of catalysis originated by Balandin.[19]

Earlier supporting evidence arose from more indirect attempts to relate activity to crystal face. It was observed that the activity of cyclohexane dehydrogenation parallels the intensity of X-ray reflections from the (111) crystal face, but not from other faces.[20] Again exposed (111) planes of nickel films have been shown by electron diffraction to be active in benzene hydrogenation, but not the (110) plane.[21]

However not only the interatomic distance differs from one crystal plane to another. It has been known for some time that the electronic work function also varies in this way.[22] This fact is the basis of the Field Emission Microscope.[23] In this instrument electrons emitted by a metallic tip are allowed to fall on a scintillating screen, there giving rise to dark and light areas of varying intensities corresponding to the emitting crystal planes. Adsorption causes changes in work function and so, on such a tip will give rise to changes in the emission pattern on the screen.

The field emission microscope has been used to demonstrate preferential adsorption on certain crystal faces.[24] The technique has been limited to the study of adsorption of simple molecules such as hydrogen and nitrogen on tungsten.[25] However it has recently been extended to include certain organic molecules, among them ethylene.[26]

Further to this question of heterogeneity, evidence of the following kind is being accumulated. Two forms of hydrogen adsorption have been observed on non-stoichiometric cobalt oxide.[27] They are a fast reversible adsorption followed by a slow irreversible type. Two types of hydrogen adsorption have also been observed on graphite,[28] one at - 196°C and one in the range 600° - 750°C. This has been explained by Thomas in terms of two types of adsorption site on the crystal edges.

As has been shown different energetics of adsorption on different sites give rise to different rates of adsorption. However they may result also in different modes of adsorption. This possibility has been demonstrated by infra-red absorption studies of adsorbed species. The adsorption of carbon monoxide on tungsten, palladium and nickel occurs in two forms.[29] One is single site adsorption and the other involves two adjacent sites in a bridge structure. Flash desorption and field-emission[30,31] studies on pure tungsten surfaces show that nitrogen is

adsorbed in three distinct ways.

It is indicated that in deuterium exchange with propane, pentane and hexane on palladium and rhodium films that in addition to the earlier known mono-adsorbed and di-adsorbed species [32] an tri-adsorbed [33] intermediate is involved in the mechanism. Yates and Lucchesi [34] have observed two forms of acetylene and methyl-acetylene adsorption on alumina at room temperature. The technique used here was infra-red spectroscopy.

There is a considerable body of evidence for varying methods of ethylene adsorption on surfaces. Most of the infra-red studies have been of supported catalysts. Little, Sheppard and Yates [35] have studied ethylene adsorption on palladium and nickel supported on porous silica glass. They found evidence for both olefinic and paraffinic carbon-hydrogen bond stretching frequencies. These observations are in agreement with those of Eischens.[36]

Changes in the electrical and magnetic properties of metal films during adsorption have long been observed. [37] These facts have given rise to the concept of the Electronic Factor in catalysis in which the importance of the electronic state of a surface is stressed rather than the simple geometric array of surface atoms. It is useful to distinguish between electronic and geometric effects in discussions of catalytic activity [38]

although the distinction is not one of kind. It can hardly be doubted that interatomic distance is itself electronic in its underlying nature.

Measurements of the conductivity of metal films have been studied by Zweitering, Koks and Van Heerden.[39] Up to about half coverage of the surface they found evidence for the formation of four bonds for every ethylene molecule adsorbed. Beyond this point it appeared that fewer bonds were being formed per molecule adsorbed. Selwood [40] has studied the changes in magnetic properties attendant on the adsorption of ethylene on silica-supported nickel catalysts. Again evidence for four bond formation was obtained. At 0°C however the adsorption came about on formation of two bonds. This type of adsorption decreased as the temperature was raised and the occurence of four bond formation increased.

Thus we have evidence that surfaces are energetically heterogeneous, that this heterogeneity results from the different properties of different crystalographic planes and that it gives rise, not only to differing rates but also to differing modes of adsorption.

Since differing modes of adsorption occur on the same catalyst it may be enquired if the resulting adsorbed complexes are all reactive.

Selwood [40] has shown that 46% of the adsorbed ethylene species could not be removed by hydrogen in his experiments with silica-supported nickel catalysts. Eischens [36] has demonstrated the removal of the olefinic carbon-hydrogen stretching frequencies from the infra-red spectra of the adsorbate. It was not known however whether removal from the surface actually took place.

Attempts to obtain a measure of the extent of reactive species as a percentage of the total adsorption have been made by Thomson and co-workers. It was shown in the Rosenmund reaction[41] and in the hydrogenation of vinylacetic and crotonic[42] acids that the active area of the catalysts involved was a very small percentage of the adsorbing area. This was done by showing that the amount of labelled reactant adsorbed was substantially independent of the presence of thiophen, in sufficient quantity to poison the reaction. In this work the adsorption measurements were obtained separately from the reaction rate measurements.

The importance of measuring adsorption during surface catalysis has been emphasised by Tamaru.[43] Simultaneous measurement of reaction rate and extent of formic acid adsorption on silver, copper and nickel catalysts [44] showed that adsorption had taken place over about 10% of the available surface. The adsorption measurements were carried out in a closed circulating system. From the amount of reactant introduced to the system

and the pressure and composition of the circulating gases, the extent of formic acid adsorption on the surface was calculated. This method however does not distinguish between catalytically active and non-catalytic adsorption.

Wishlade [45] in a study of hydrogenation of ethylene on evaporated nickel film was able to measure the reactive adsorption as a percentage of the total, and to do this under reaction conditions. The hydrogenation and subsequent removal to the gas phase of pre-adsorbed ethylene - C - 14 was observed by a Geiger-Muller tube on addition of a mixture of non-radioactive ethylene and hydrogen. The fall in radioactivity on the surface over the initial value was proportional to the fraction of catalytically active sites present. 40% of the surface was found to be active.

It was proposed in this work to measure reactive surface areas under reaction conditions.

It was decided therefore to extend the observations of Thomson and Wishlade to a series of catalysts to ascertain whether or not this type of surface heterogeneity was in any way general. If it was found to be so, then a correlation between the percentage active adsorption and the physical and chemical properties of the metals involved was to be attempted. It was intended to compare the observed active areas withthe results of infra-red spectrographic results and exchange studies with respect to the

extents of the various adsorbed species. The aim here being to ascertain which species were active. To sum up, the active area of a catalyst could be used as a new parameter in the study and discussion of catalysis. It was hoped that more success would attend attempted correlations involving this parameter than had attended earlier attempts involving the total surface area or the total chemisorption area.

Supported catalysts were chosen for study, partly because a more extensive survey could in this way be carried out and partly because of a desire to study these particular catalysts. A great deal of work has been done on these catalysts owing to their industrial importance and the less stringent vacuum conditions required in their preparation. However fundamental studies of the mechanism of catalysis are very often carried out on evaporated metal films, or at any rate on pure metals since there is then no need to consider the effect of the support.

The action of the support is nevertheless worthy of study itself. In the early days the support was thought of as a means of dispersing the metal so as to obtain a large surface area. It was also considered to stabilise this large area and help to prevent sintering. However there is evidence suggesting electronic interaction between the metal and support,[46] the

effect of the support being much greater than would be expected from a simple maintenance of surface area.

Investigations have been undertaken to discover the effects of changing the metal-support ratio and also the type of support. Chaston and Sercombe [47] have shown that palladium-charcoal catalysts have maximum hydrogenation activity when they contain 4-5% palladium. The effects of various silica supports on the catalytic activity of nickel have been investigated.[48] Again it has been discovered that the maximum dehydrogenation of cyclohexanol is obtained on iron-alumina catalysts containing 75% iron.[49] In the range 25-100% iron the activation energy doubles. Such results as these are very difficult to interpret.

It was therefore thought, with a view to future work, that if a method of measuring active areas could be developed for supported catalysts these measurements could be of importance in attempting to ascertain the agency through which changes in support alter catalyst characteristics. It was not, however proposed to enter this study in the present work but rather to maintain constant support and metal support ratio and to study variation in the catalysts as the metals themselves were changed.

The system finally chosen for study was the hydrogenation of ethylene over alumina supported catalysts. The procedure involved the direct monitoring of the surface with a G.M. tube

while the surface was gradually saturated with ethylene - C - 14. The fate of this adsorbate was then observed with the G.M. tube after admission to the catalyst of an equimolar mixture of ethylene and hydrogen. It was also proposed to study the extent of ethylene exchange between the surface and the gas phase by the same means and finally to discover the effect of hydrogen alone on any retained adsorbate found after the hydrogen or exchange reactions were complete.

Since it was desired to measure the extent of unreactive adsorbate it was important to choose a reaction, the products of which were removed to the gas phase, for undesorbed product cannot be distinguished by the method from unreacted adsorbate. The ethylene hydrogenation reaction is well documented [50] and would appear to fulfil this condition.

CHAPTER 2

APPARATUS AND MATERIALS

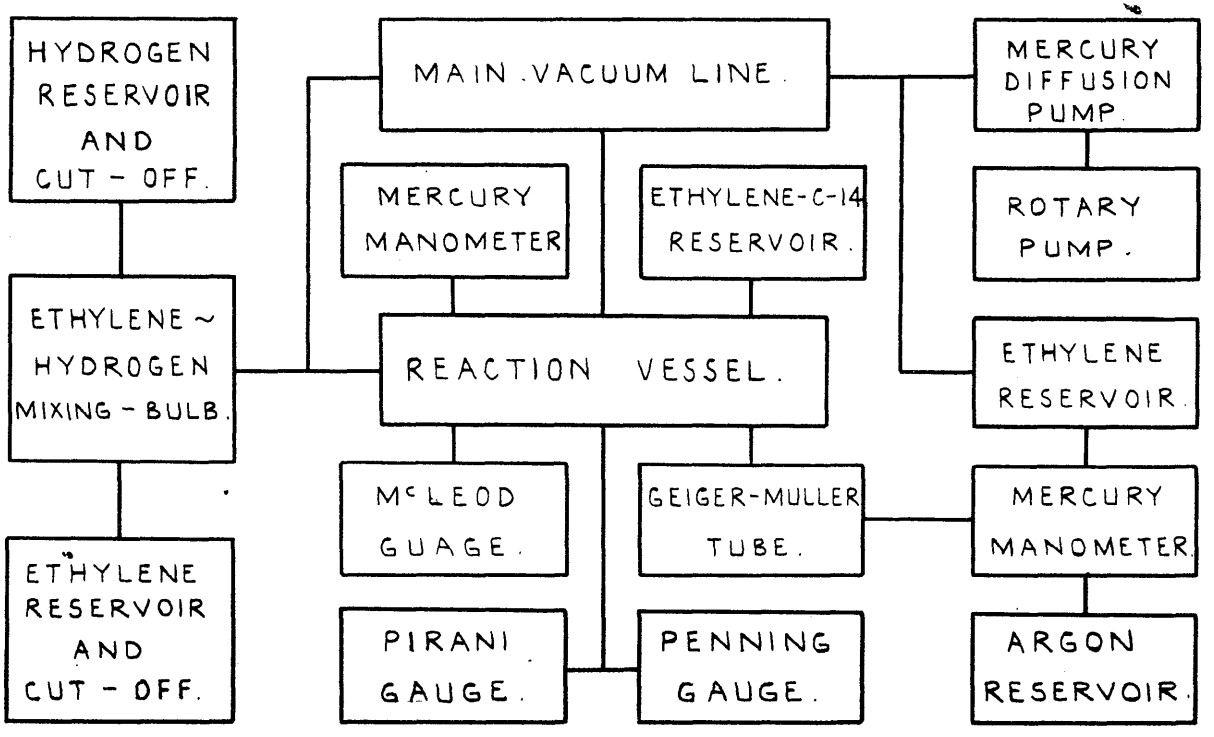
2.1. General description of apparatus

Since supported catalysts were to be studied the apparatus had to be equipped with catalyst reducing facilities. Storage had to be provided for ethylene, ethylene - C - 14, and hydrogen. Extremely fine control of the quantities of ethylene - C - 14 admitted to the catalyst was required for adsorption studies. A G.M. tube was required for these studies. The apparatus also had to include equipment for premixing the ethylene and hydrogen in equimolar amounts before admission to the catalyst, together with pressure measuring devices to follow subsequent reaction. Finally a gas handling system for counter filling gases was required. The apparatus which was designed to fulfil these requirements is shown in the block diagram, fig. 1.

Hydrogen could be passed through the reaction vessel which was fitted with a furnace for 'in situ' reduction of catalysts, and a G.M. tube for monitoring the activity on these catalysts. Pressure measuring devices comprising of a mercury manometer, McLeod, Pirani and Penning gauges were connected to the reaction vessel.

The gas handling unit consisting of reservoirs for hydrogen and ethylene, and a mixing bulb, was connected to the reaction

FIG 1.


HYDROGEN RESERVOIR AND CUT - OFF.
MAIN VACUUM LINE.
MERCURY DIFFUSION PUMP.
MERCURY MANOMETER
ETHYLENE-C-14 RESERVOIR.
ROTARY PUMP.
ETHYLENE ~ HYDROGEN MIXING - BULB.
REACTION VESSEL.
ETHYLENE RESERVOIR.
McLEOD GUAGE.
GEIGER-MULLER TUBE.
MERCURY MANOMETER.
ETHYLENE RESERVOIR AND CUT - OFF.
PIRANI GAUGE.
PENNING GAUGE.
ARGON RESERVOIR.

vessel and to the main vacuum line. These reservoirs were connected to the mixing bulb through mercury cut-off valves. These valves were chosen rather than conventional taps to prevent contamination of the stored gases over long periods. Similarly the reservoir for ethylene - C - 14 was fitted with a mercury cut-off valve with the added advantage in this case of fine control over gas flow.

The counter filling system consisted of reservoirs for argon and ethylene and a mercury manometer.

The various sections were connected to the main vacuum line and the pumping unit, which consisted of a mercury diffusion pump and a rotary backing pump.

2.2. Pumping System

The pumps were supplied by Edwards High Vacuum Limited, The diffusion pump was model IM2B. This is a mercury diffusion pump, and it was chosen in preference to an oil pump since mercury is not susceptible to oxidation and cracking damage, as is oil. The diffusion pump was connected to the main vacuum line through a trap cooled in liquid nitrogen, to prevent the entrance of mercury vapour to the apparatus.

A second cold trap was interposed between the diffusion pump and the rotary pump, model 1350, to prevent oil from

contaminating the former. The outlet from the rotary pump was connected to the laboratory exhaust system so that radioactive gases could be carried away safely.

As many connections as possible were arranged between the various components of the apparatus and the main vacuum line so as to facilitate evacuation. The main vacuum line was of large diameter, 2.5 cm and was connected to the pumps through 6 mm diameter glass vacuum taps of conventional design. These 6 mm taps, and the 4 mm taps used elsewhere on the apparatus, were greased with Edwards' Apiezon N, code number H.230/11. The vapour pressure of this product is lower than 10^{-6} mm at room temperature.

A secondary vacuum line was also provided for operation of the mercury cut-off valves and the McLeod gauge.

2.3. Pressure Measuring Devices.

Pressures of the order of 10^{-5} mm were to be expected on evacuating the apparatus and the 'Speedivac' Pirani-Penning type vacuum gauge model 2A was used for this range. In this were combined under one control unit the standard model 4B Pirani gauge and the standard model 5 Penning gauge. Both gauges were calibrated only for dry air, but were claimed to

be accurate for most purposes under normal vacuum conditions where small quantities of other gases and water vapour are present. As it was not intended to use them for anything other than general monitoring of the apparatus, no further calibration was made.

2.4. Pirani Gauge.

This depends for its operation on the thermal conductivity of a gas: at low pressure this decreases linearly with pressure. Thus the change in temperature of an electrically heated tungsten filament may be used to measure ~~temperature.~~ pressure. The tungsten filament has a high resistance-temperature coefficient so that any change in temperature produces a large corresponding change in resistance. The filament formed one arm of a Wheatstone bridge circuit and the change in resistance produced an out-of-balance current which was read on the meter of the control unit. The pressure range of the Pirani gauge was $1 - 10^{-3}$ mm.

2.5. Penning Gauge.

Such a gauge consists of an outer cylinder which acts as a cathode. Within this cylinder is placed an anode ring. Under vacuum conditions a glow discharge may be sustained by a high d.c. potential across the electrodes. The current in

this discharge is a function of the gas pressure. Electrons emitted from one side or other of the cathode are accelerated through the anode ring and so are set in oscillation on either side of the anode plane before being finally collected at the anode. The electrons produce positive ions, by collision with the gas molecules, which are then collected at the cathode and registered as a current. This current is a function of gas pressure.

If the electrode system is placed in a strong magnetic field the electrons follow helical paths, travel further, and therefore tend to produce more ionisation by collision. This extends the low pressure end of the range of pressures measurable by the gauge. The gauge used here had a range of $10^{-2} - 10^{-5}$ mm.

Used together these two gauges enabled pressures to be read in the range $1 - 10^{-5}$ mm.

2.6. a McLeod Gauge : Introduction

It was decided to measure gas pressures during the build-up of the initial monolayer of ethylene on the various catalysts. The gauge is shown in fig. 19.

Since the gauge depends for its operation on the application

of Boyle's Law it should only be used for ideal gases. However since deviations from ideal behaviour are least at low pressures such a gauge could be used to measure low pressures of ethylene.

Gas remaining in the bulb after evacuation may be compressed into the closed capillary limb to a pressure equal to the difference in height between the levels of mercury in that limb and in the compensating limb. Suppose the difference in level is h cm then the pressure of the trapped gas is h cm. The volume of this gas is H.a.cm ^{3} where H cm is the height of the gas column above the mercury level and a cm ^{2} is the cross-section area of the capillary tube. Then if V cm ^{3} is the volume of the gauge and therefore of the gas at the unknown pressure p cm we have by Boyle's Law that,

$$p = \frac{h.\ H.\ a.}{V}$$

It was necessary therefore to calibrate the cross-section area of the capillary tube and the volume of the gauge. The values of h and H were measured by means of a cathetometer each time a pressure was to be computed.

2.6.b McLeod Gauge: Calibration.

Before calibration, the entire gauge was filled with chromic acid solution and left overnight, the chromic acid

finally being rinsed out with distilled water.

After being dried in an oven at 100°C the gauge was calibrated by being weighed empty and then filled with distilled water, at 22°C, to the end of the bulb constriction tube. The volume V was then computed to be 34.62 ml at 22°C.

The capillary tubes in the gauge were constructed from 0.15 cm diameter tubing, supplied by Chance Brothers Limited, Birmingham, which had a tolerance of 0.1 mm in bore and a low coefficient of expansion. The bore diameter was checked by introducing a thread of mercury, measuring the length of this thread with a moving microscope, and finally weighing the mercury.

In this way the diameter area was computed to be 0.153_1cm.

2.6c McLeod Gauge Discussion

Accurate use of the gauge depends on the calibrations described and on the accuracy with which h and H can be measured.

These measurements are affected by capillary depression which increases with decreasing capillary diameter. Capillary depression is caused by variation in angle of contact between the mercury and the glass. This angle can vary between 30°

and 60° in a gauge in which mercury and glass are perfectly clean. Rosenberg [51] has shown that roughening the inside of the capillaries reduces this error.

An advantage in using Chance's Veridian precision bore tubing is that in its construction a mandrel is finally dissolved out from the tubing and so its inside surface is roughened.

Capillary depression can be reduced by increasing the tube bore. However if this is done the values of h and H, which have to be measured each time, also become smaller so that a compromise has to be agreed. In this way 0.15 cm diameter tubing was chosen.

This gauge could be used to measure pressures of the order of 10^{-2} mm and could measure down to 5×10^{-4} mm.

2. 7. Mercury Manometer.

A fourth pressure measuring device incorporated in the apparatus was the mercury manometer which was designed to follow pressure changes in the reaction vessel during the hydrogenation of ethylene. It was also used to measure pressures in the hydrogen-ethylene mixing flask M fig. 2 when the reactants were being mixed. This manometer was capable of measuring pressures up to one atmosphere.

FIG. 2.

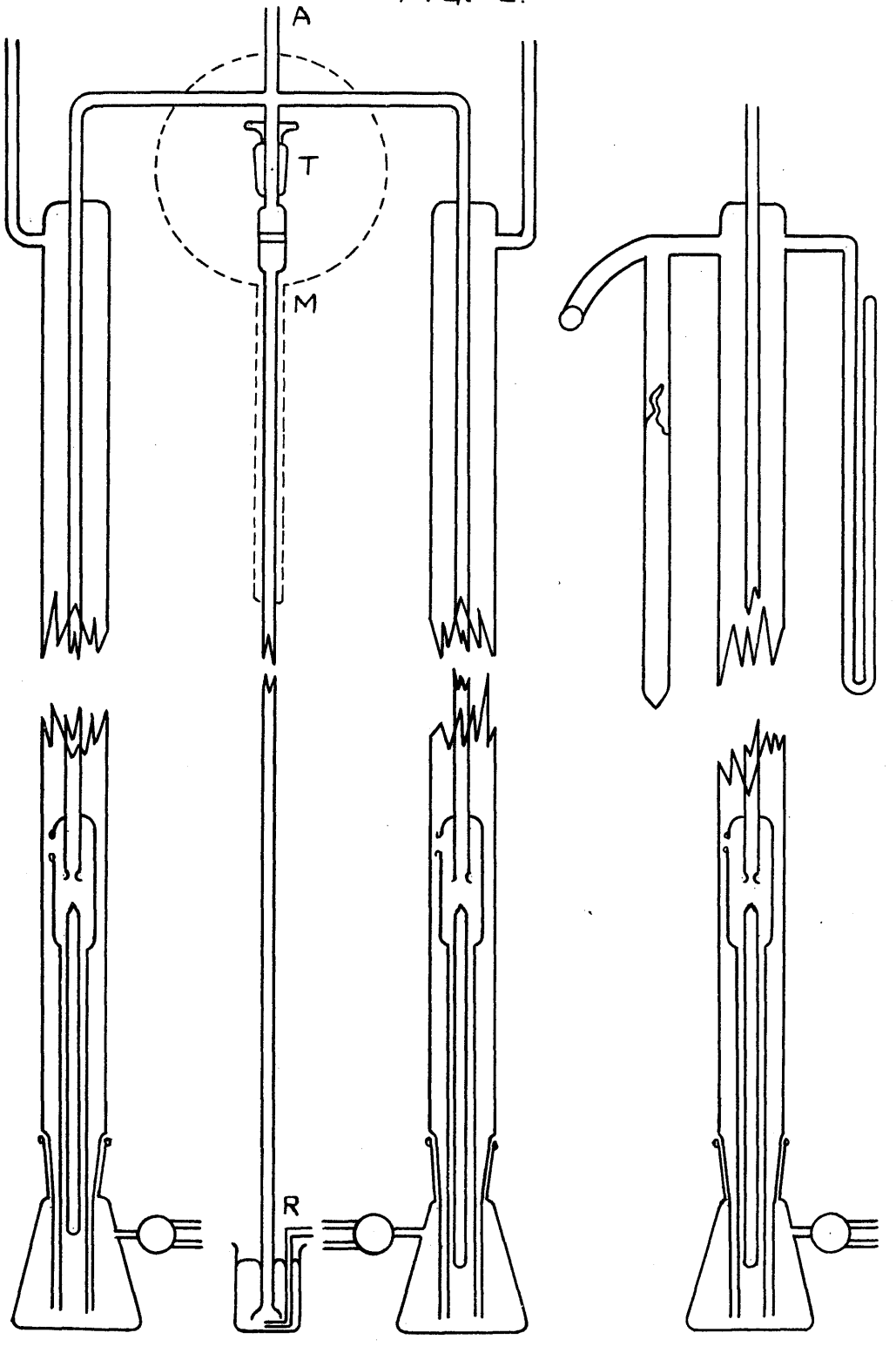
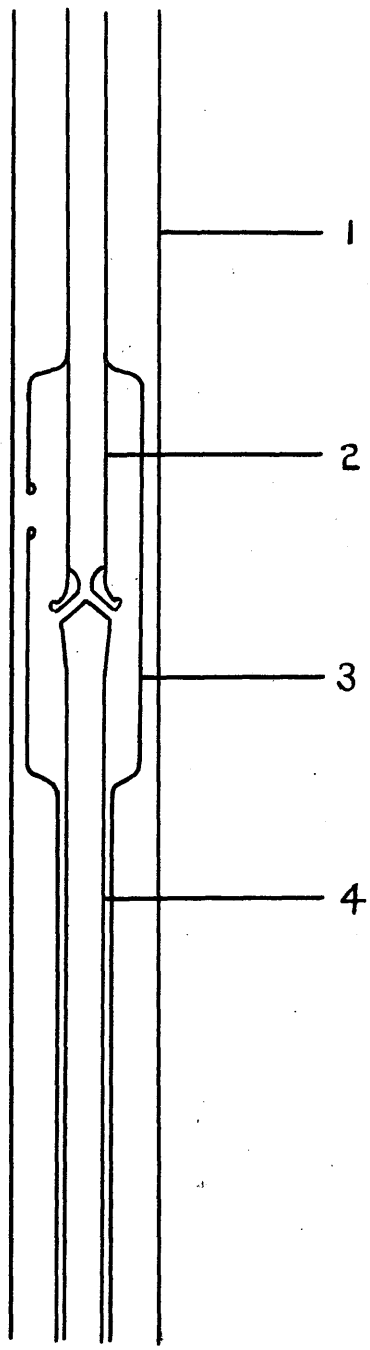


FIG. 3.



of the outer tube. The outer tube was connected to a 2 l storage bulb and the inner to the rest of the apparatus. The bottom end of the outer tube fitted into a 250 ml. conical flask by means of a B.24 cone. It was extended beyond the B.24 cone almost to the bottom of the conical flask which contained doubly distilled mercury. The bottom end of tube 2, the inner one, passed for some distance into the wider tube 3 through a ring-seal and terminated in a thickened end. Tube 3 extended to near the bottom of the conical flask, the lower portion being narrower than the upper, to act as a guide for the float, 4. The top end of this float was ground with carborundum powder to fit into the thickened end of tube 2. There was a hole in the wide top portion of tube 3 by means of which the inner and outer tube systems could be connected when the float was not in contact with the ground glass seating.

The 250 ml. conical flask was fitted with a three-way tap and could be connected by it to the secondary vacuum line or to the atmosphere. This provided a means of raising or lowering the mercury level in the tube system. If the mercury was caused to rise inside the tubes it took the float with it and so closed the valve.

Initially then, with air filling the entire system the

valve is open and the mercury level in the tubes is the same as that in the flask. The tubes, and so the storage bulb may then be evacuated. As the pressure falls in the bulb and tubes, the mercury level rises in the said tubes and if allowed to continue would eventually close the valve making further evacuation impossible. This may be prevented by opening the conical flask to the secondary vacuum line so reducing the pressure on the mercury surface within the conical flask. In this way the storage bulb may be pumped out.

The storage bulb could be filled through the inner tube when the valve was open. It could not of course be filled to atmospheric pressure, for then the valve could not be closed.

The pressure to which the reservoir can be filled is atmospheric pressure less the head of mercury when the level is just above the valve, where it has to be to seal off the reservoir from the rest of the apparatus. If the pressure in the reservoir is less than this limiting pressure then by opening the conical flask to atmospheric pressure the mercury level may be raised further above the valve. Atmospheric pressure less this new head of mercury is the new pressure of gas in the reservoir. Thus the pressure in the reservoir may be measured at any time.

Atmospheric pressure on the mercury surface in the conical flask closes the valve. Thus leakage through the only conventional tap associated with the reservoir will not lead to contamination of the stored gas since there is atmospheric pressure on both sides of it when the valve is closed.

Gas could be maintained in the storage bulb without the float simply by raising the mercury level as previously described. The advantage of the float is that it enabled gas to be removed from the storage bulb in a controlled manner. For, when the mercury level is lowered, by connecting to the secondary vacuum line, it drops below the level of the valve before the valve faces actually part contact. If this situation be maintained the stored gas diffuses out in a slow controlled manner. On raising the mercury level above the valve again an immediate seal is effected.

Three such cut-off valves were included in the apparatus. One each for the 2l reservoirs for hydrogen and ethylene and one for the reservoir which contained the ethylene - C - 14. This third cut-off valve was connected, as shown in fig.2, to a manometer and a phial containing ethylene - C - 14.

These phials, provided with break-seals, were supplied by The Radiochemical Centre, Amersham and contained ethylene of

activity 0.1 m C, code number C.F.A. 141. The radiochemical purity was 99%.

When required the break-seal could be broken by raising a ball-bearing, diameter 5/16 inch, by means of a magnet from the side arm shown in fig. 2 and dropping it on the break seal.

The ethylene - C - 14 was then controlled by the cut-off in the manner described.

2. 9. Filling of Reservoirs With Hydrogen and Ethylene.

These gases were supplied by British Oxygen Company Limited.

The inner tubes of the two cut-off valves were both connected to a vertical tube fitted with a No. 4 sinter at the top end. The lower end of this tube dipped into a beaker containing mercury so that entry to the tube could be effected only from beneath the mercury surface. A second tube dipped into the mercury in the beaker. This tube was free to rotate so that its lower end could be placed under the lower end of the vertical tube. The arrangement is shown in fig. 2. Molten paraffin wax was poured over the mercury surface in the beaker and allowed to set. This was done to prevent mercury vapour escaping into the laboratory atmosphere.

To fill a reservoir with hydrogen, the rotateable tube R, fig. 2, was attached to the outlet tube of a trap containing activated charcoal which was immersed in liquid nitrogen. The inlet of the trap was connected to a supply cylinder of hydrogen

This trap was designed to remove contaminating gases from the hydrogen as it flowed from the cylinder to the reservoir.

During the first five minutes, in which the hydrogen was flowing, the tube R fig. 2 was turned aside from the inlet tube and the gas displaced from the system allowed to escape through a hole in the paraffin wax cover. This process removed air from the system. Tube R, was then placed under the filling tube and hydrogen allowed to pass through the sinter into the reservoir.

As the reservoir gradually filled the mercury level in the filling tube gradually fell below the sinter. Atmospheric pressure less the head of mercury in the filling tube equals the gas pressure in the reservoir. In this way a check can be kept on the gas pressure in the reservoir. It is important not to exceed the pressure represented by the head of mercury above the valve in the other cut-off otherwise hydrogen will pass through it also and enter the other reservoir.

When the reservoir had been filled to this pressure limit with hydrogen, the valve was closed and the excess gas in the filling tube and inner tube of the cut-off valve was pumped away.

The ethylene supplied by British Oxygen Company Limited was treated in the following way before being admitted to the reservoir. With both cut-off valves closed ethylene was passed

from the supply cylinder into the gas mixing bulb M, fig. 2. This was a 327 ml. bulb, calibrated before assembly in the apparatus, by weighing empty and then full of distilled water. The cold finger attached to M, fig. 2, was then surrounded with liquid nitrogen to condense the ethylene. When this had been done any residual gas was pumped off before the liquid nitrogen was removed. The cut-off valve was then opened to allow the ethylene to evaporate into the reservoir. Before the cold-finger reached room temperature the valve was again closed and the mixing bulb evacuated to remove water vapour. This process was repeated until the reservoir was filled with ethylene.

2. 10. Mixing of Hydrogen and Ethylene.

Since it was proposed to admit a gas mixture to the catalyst, hydrogen and ethylene were mixed before they were admitted to the reaction vessel.

The reservoir containing ethylene was opened to the mixing bulb, M fig. 2, which in turn was opened to the manometer, M fig. 19. Ethylene was allowed to fill the mixing bulb to a pressure of about 20 cm. The reservoir cut-off valve and tap T, fig. 2, were then closed and the excess ethylene in the connecting tubes was pumped away. Meanwhile, the ethylene was condensed into the cold-finger of the mixing bulb, M fig. 2.

The reservoir containing hydrogen was now opened and hydrogen was allowed to fill the mixing bulb to a pressure equal to that previously read for ethylene.

The liquid nitrogen was then removed from around the cold-finger and the gases allowed to mix. The mixture was allowed to stand for 10 minutes before being admitted to the reaction vessel.

The use of liquid nitrogen for ethylene condensation prevents the hydrogen in the reservoir from becoming contaminated with ethylene.

2. 11. Storage of Gases for G - M Counter Filling.

Since a G - M tube was to be used in this research it was necessary to build a G - M tube filling section incorporating storage facilities for the filling gases. This can be dealt with more appropriately, however, in the section on the G - M tube.

2. 12 a. Catalyst Vessel : Description.

The size of the catalyst vessel was governed by the need to keep the G - M tube away from the furnace used for reduction of the catalyst at 500 $^{\circ}$C. This resulted in a vessel 60 cm long with a volume of 887 cm ^{3}. This was determined by gas expansion from the known volume of the mixing flask M, fig. 2.

Provision had to be made for moving the catalyst holder from the reduction region under the furnace to the G - M tube region for monitoring surface radioactivities and for moving it back

and forth during this monitoring for determination of surface and gas phase count-rates.

It was decided that the simplest thing to do was to attach the catalyst vessel at its mid-point to the apparatus by means of a ball and socket joint. This arrangement permitted rotation of the catalyst vessel so that the catalyst holder could slide back and forth as required.

The catalyst holder was inserted through a B.34 cone and socket at the end opposite the furnace. The catalyst vessel was connected to two taps so that hydrogen could be passed through it and over the heated catalyst to effect reduction.

2..12 b. Catalyst Vessel Furnace.

The furnace was designed to slip neatly over the catalyst vessel. The resistance tape was wound on a 7 inch long brass cylinder of diameter 1.75 inches.

It was assumed that 500° - 600° C could be attained from a furnace of 350 W, so that 5.14 yards of Nichrome tape of 34.55 ohms per yard.resistance would be required. The furnace was controlled by a Sunvic simmerstat type E.R.C. supplied by A. E. I. Limited. The setting required to give 500° C for reduction was obtained by use of a 550° C thermometer.

2. 12 c.G. M. Tube.

The G - M tube and its relation with the catalyst holder are discussed in section 3.10.

The final arrangement of the catalyst vessel, furnace F, counter G - M and movable catalyst holder H are shown in fig. 16. The relation of catalyst vessel to the other measuring devices is given in fig. 19.

2. 13a. Catalysts: Description

In this section will be described the supported catalysts [52] and the method employed to cause them to adhere to the catalyst holder.

All the catalysts used were 5% metal supported on alumina. The metals studied were nickel rhodium, palladium iridium and platinum. With the exception of the nickel catalyst they were supplied by Johnson, Matthey and Company, Limited. They were of impregnation type, being produced by evaporation of the appropriate salt solution over alumina. The nickel catalyst was prepared from Analar nickel nitrate solution. The support used in this case was type A alumina supplied by Johnson, Matthey and Company, Limited. After being dried in an oven at 100° C this catalyst was calcined for 6 hours at 500° C to form the nickel oxide.

Care was taken to avoid contamination of these catalysts. They were stored in screw-top bottle which were opened only in the weighing room and then only long enough to remove the required sample.

2. 13b. Dispersion Of The Catalysts.

As outlined earlier the catalyst holder has to be moved back and forth with respect to the G - M tube in order to obtain the value of the surface activity as the difference between a count rate due to the gas phase activity plus the surface activity and the gas phase activity alone.

It will be impossible to compare one surface count with another unless the geometric relationship between the catalyst surface and the G - M tube is invariant when the two measurements are made. For this reason the holder must always be brought to the same position relative to the G - M tube and of course it will not be sufficient to deposit the catalyst on the holder as a powder as this would be free to move relative to the holder and so relative to the G - M tube.

How the first condition is satisfied will be explained in section 3.10. Meanwhile we will deal with the second condition.

Clearly the catalyst has to be made to adhere to the surface of the catalyst holder. Early attempts to do this consisted of roughening the surface of the holder by rubbing with carborundum powder, then spreading the catalyst out on the holder as a thin slurry with water. However when this was dried out at 100° C the catalyst was always found to be quite

loose. Attempts were also made with rough silica glass holders but without success. Reference is made by Schuit and van Reijen [53] to the use of montmorillonite for the purpose of making catalysts adhere to glass. When the catalyst was mixed as a slurry with water and montmorillonite it could be spread evenly over the holder, and when dried out at 100°C was found to adhere firmly to it.

The catalyst had to be spread out thinly to increase the chance of adhesion to the glass. However this brought benefits in other directions as it would be expected to reduce self adsorption of the β - particles from the adsorbed ethylene in the sample and also to expose more catalyst surface to the gas phase.

2. 13c. Sodium-free Montmorillonite.

The montmorillonite supplied by the Fullers' Earth Union Limited is the sodium-calcium variety, Wyoming Bentonite. This had to be freed of alkali and alkali earth elements for use in the present context.

This was done in the following way. An attempt was made first of all to exchange the sodium and calcium ions for hydrogen ions by passing 0·1N hydrochloric acid over the montmorillonite. The flow rate in this system was however most unsatisfactory. It was therefore decided to reflux the montmorillonite with

500 ml. of 0·$\overline{1}$ N hydrochloric acid in a 1 litre round bottomed flask.

Refluxing was continued for 8 hours during which time the exchange process was followed by withdrawal of aliquots of the supernatent liquid and back titrations with standard sodium hydroxide solution. The cation exchange capacity of the material was found to be 80 milliequivalents per 100 g, in good agreement with the supplier's specification of about 80-90 milliequivalents per 100 g. The material was then centrifuged and washed with distilled water until the washings were neutral to litmus. It was assumed that if the excess hydrogen ions had been removed so also would any sodium and calcium ions which otherwise may have adhered to the solid when this was dried out.

CHAPTER 3

COUNTER DEVELOPMENT

3. 1. Introduction.

Since the proposed method of study in this research involved direct monitoring of the adsorption on surfaces of ethylene - C - 14 it was necessary to consider how this was to be effected.

The first problem arises from the low energy of the β-particle disintegration of the carbon - 14 nucleus, the maximum energy for this process being only 0.1555 MeV. Detection therefore requires special end-window counters with very thin windows or alternatively scintillation counting. If higher counting efficiency is required gas counting techniques may be adopted, but this latter procedure involves mixing the gas to be estimated as a constituent of the counter filling gases. Neither scintillation nor gas counting lend themselves to the present problem. Nor at first sight is end-window counting attractive. Since the energy of the β-radiation in question is so low a large detection area is required and this forces consideration of the second difficulty, viz the mechanical strength of the window for

admission of β -particles to the counter. A window of large area which is very thin is difficult to support.

Mechanical strength is required not only to enable the G - M tube to be evacuated and filled but also to enable it to withstand subsequent pressure differences when in use, as for instance when the reaction vessel in which it is situated is evacuated following reduction of a catalyst.

3. 2. Cylindrical Counter.

Initially it was thought that the cylindrical thin windowed G - M tube employed by Thomson and Wishlade [45] would serve the present purpose. This has been described elsewhere. [54] It consists of a cylindrical copper cathode with hexagonal close-packed circular holes in the walls. Down the axis is stretched an anode wire of tungsten which passes through glass end pieces to insulate it from the cathode. The curved surface of the cylinder is covered with 4.54 mg/cm^2 Mellinex film which is sufficiently thin to be partially transparent to carbon - 14 β -particles.

The catalyst holder most appropriate for use with this G - M tube was itself a cylinder, the catalyst adhering to the inside curved surface, so that it may be monitored with the G - M tube placedinside the holder.

This design appears to overcome both difficulties. Not

only do we have a large detecting surface, the area of curved surface may be made as large as necessary, but also in Mellinex, a material sufficiently strong to withstand the pressure variations to which it is to be subjected.

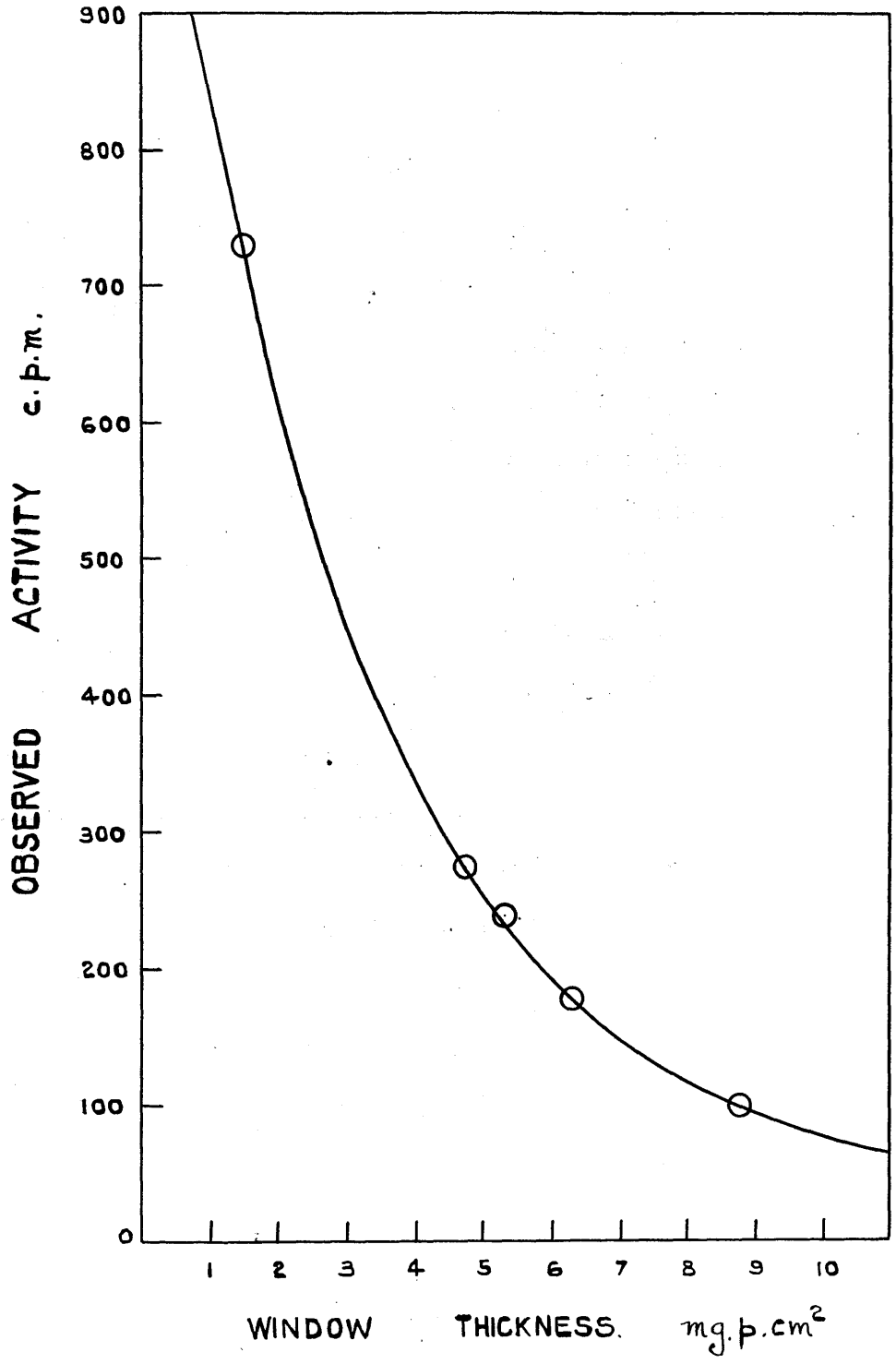
Accordingly such a G - M tube was constructed and its characteristics observed. It was noted however that when the tube was being evacuated and filled, the flexing of the Mellinex was considerable. This flexing also occurred when the volume surrounding the tube was evacuated. The result of this was the development of leaks in the bonding regions of the Mellinex film.

This situation led to a re-consideration of the end-window counter, in spite of the reduction in detection area which this involved.

3. 3. The End-Window Counter.

It is well-known that mica of sufficient thinness may be used as the window material in carbon - 14 detecting tubes. The first step therefore was to discover if such a mica sample would have the required mechanical strength. It was decided to obtain a graph of β-particle absorption against thickness for mica fig. 4 and to select from this the thinnest window possible consistent with the mechanical requirements. This was done using a commercial

FIG 4


900
800
700
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400
300
200
100
0
OBSERVED ACTIVITY c.p.m.
1
2
3
4
5
6
7
8
9
10
WINDOW THICKNESS. mg.p.cm²

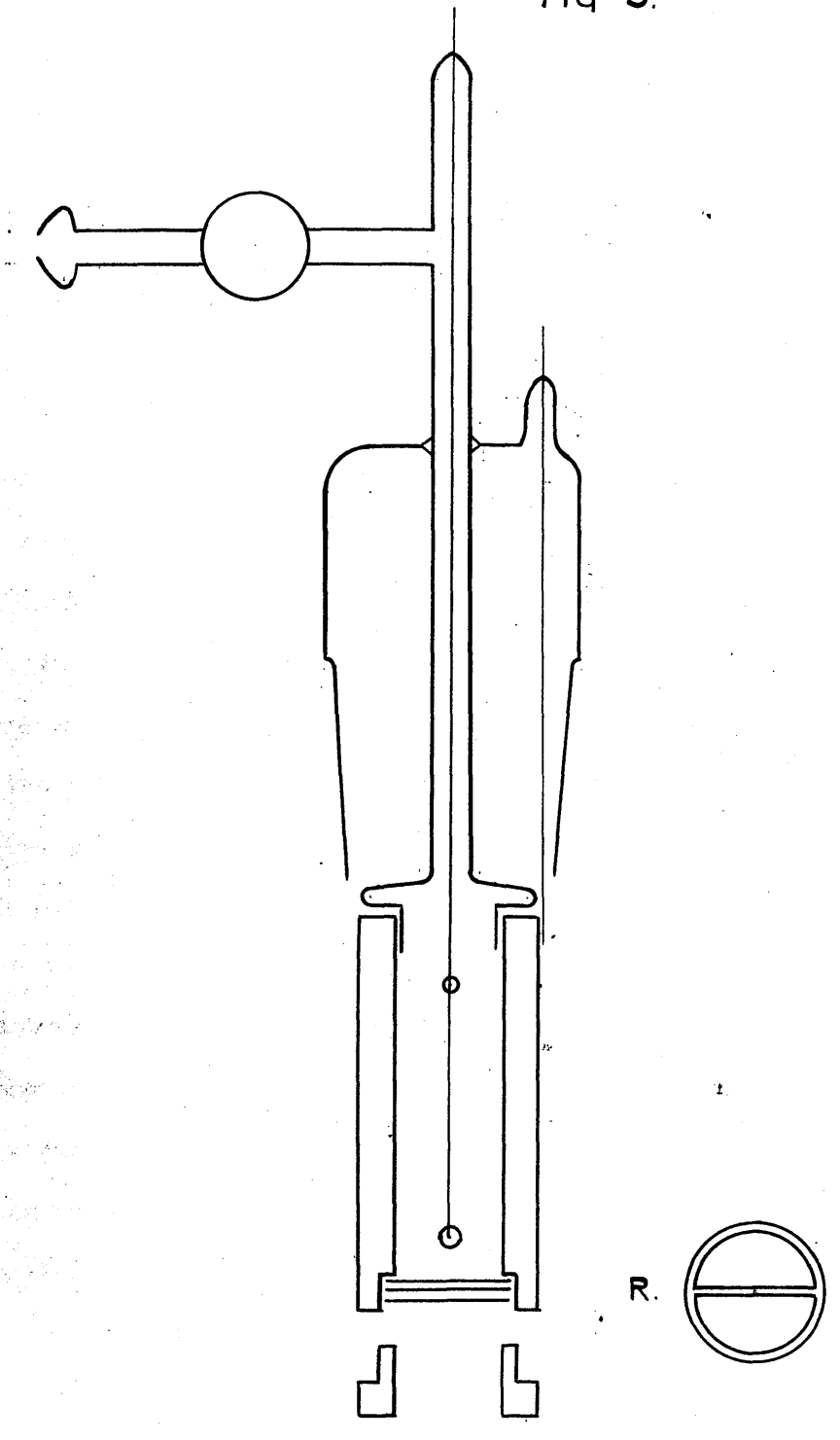
mica-windowed G - M tube, a carbon - 14 source and a selection of mica films of varying thickness which had been split from a block of mica using a pin and running water in the usual way.

It was discovered that mica of thickness 2.568 mg/cm^2 just failed to support a pressure difference of 1 atm. However this material was chosen subject to a suitable support being available for the central region of the G - M tube window.

The following design was adopted, fig. 5. The cathode of this counter, 5 cm long and 2.4 cm in diameter was of stainless steel in which a recess was cut at one end. Into this recess was placed a ring with a cross piece, R fig. 5, also of stainless steel. A circular piece of mica, cut to shape with a razor blade, was then inserted and this was followed by a second ring exactly like the first. Finally a large retaining ring, checked out to fit the recess in the cathode, was mounted as shown. The counter was assembled piece by piece using Araldite as an adhesive to ensure that no leakage was possible round the edges of the window. The window thus situated between the two rings is supported against the effects of pressure changes and this unit is prevented from being forced out or in by the retaining ring on the one hand and the cathode recess on the other.

Araldite produced by CIBA (A.R.L.) Limited, was chosen because of its good vacuum properties. Since it is an epoxy

FIG 5.



resin there are no traces of solvent to outgas slowly as with other types of adhesive.

The opposite end of the cathode was closed by a glass cap which was joined to the filling tube. The filling tube passed through a ring seal in a B.34 cone and was provided with a tap and ball joint situated on a side arm.

A 1.0 mm tungsten lead was sealed into the filling tube and passed down through the ring seal into the cathode cylinder. A thinner tungsten wire, 0.2 mm was soldered on to the end of this heavy one. This was the anode which terminated in a glass bead to prevent point discharge. The anode wire and the inside of the cathode were carefully polished with the same end in view, as any sharp points on the metal tend to give rise to spurius discharge and counts.

The anode wire was of as small a diameter as possible, consistent with reasonable rigidity which is necessary to prevent the wire sagging towards the cathode under the weight of the glass bead when the counter is in the horizontal position. A small wire diameter is necessary to provide a high potential gradient between the cathode and the wire surface so as to obtain as high a gas amplification as possible.

3. 4. Mode of Operation of G - M tube.

Gas amplification arises in the following way. When a

β -particle enters the region around the anode it is accelerated to the anode surface which is maintained at a high potential. However the arrival of one electron would not affect the potential of the anode by an amount sufficient to be measured. However under the influence of the accelerating potential, it causes gas molecules of the filling gas to be ionised by collision. The electrons produced by this process are also accelerated to the anode causing further collisions, and so on. In this way a large charge finally arrives at the anode, producing a measurable pulse. A second β -particle entering the tube during this time will not be registered as a separate event, as it will merely contribute to the first pulse. This 'dead time' during which the counter is insensitive to further arrivals sets a limit to the rate of counting. It is important therefore that the tube returns to a sensitive state as soon as possible.

However spurious discharges may occur and prevent this. When the positive ions associated with a discharge are neutralised at the cathode the resulting atoms are left with excess energy $I-\phi$ where I is the ionisation energy of the atom and ϕ the work function of the cathode. This energy is radiated as light and may cause the cathode to emit a second

electron which initiates a spurious discharge.

To prevent this a second gas is included in the G - M tube filling. This may be ethylene, bromine or alcohol vapour. The ionisation potential of this polyatomic molecule, say ethylene, is lower than that of the rare gas counter filling, say argon. Argon ions formed in the discharge can therefore capture electrons from ethylene molecules with which they collide. Thus only ethylene ions arrive at the cathode, and when they are neutralised, they use up the excess energy by dissociating into smaller molecules rather than by radiating light.

Spurious counts may also be eliminated by an external quenching circuit which reduces the potential of the anode after the arrival of each pulse, while the positive ions are being collected at the cathode.

Continuous discharge may also occur. This is maintained by photons of light produced at the anode on arrival of an avalanche of electrons. These photons, on striking the cathode are capable of releasing photo-electrons which can initiate a fresh avalanche.

The quenching gas absorbs the photons emitted from the anode before they can reach the cathode. Continuous discharge, will occur in any case, however if the potential

of the anode is raised enough. It is this process that limits the upper end of the G - M region of the counter. A counter potential should not be raised to this extent since continuous discharge destroys the quenching gas or vapour.

In our case the filling gases were argon for ionisation, and ethylene as a quenching gas, the total pressure being 12 cm and partial pressure of ethylene being 4 cm

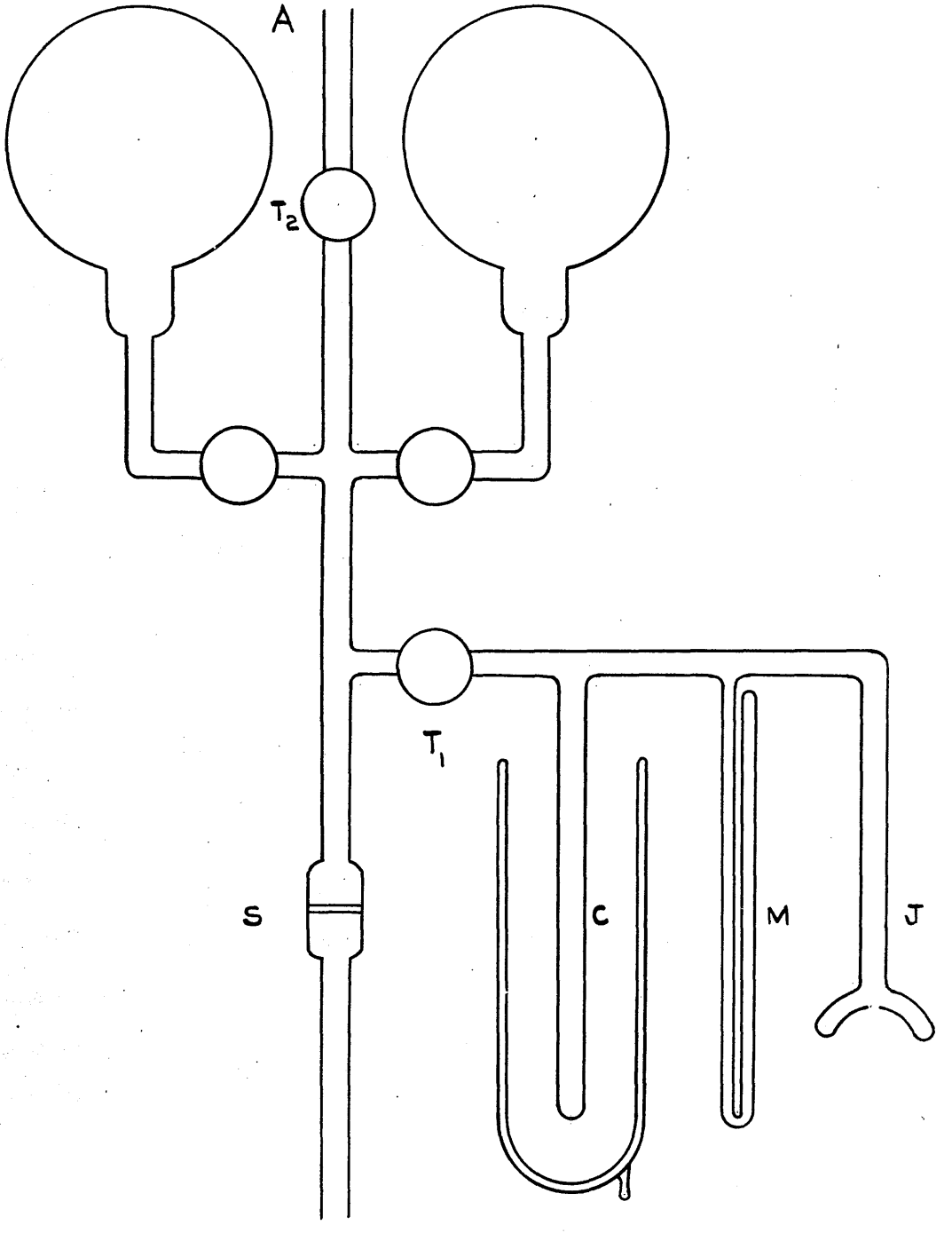
The tube was operated in conjunction with an Ecko scaler, type N529B an Ericson Telephones probe unit, type 110A, with a pre-set 'dead time' of 500 μ sec. and a quenching pulse of 240 V.

In this way the necessity of measuring the dead time of the G - M tube in order to correct observed count rates was avoided by setting it electronically at 500 μ sec, a value in excess of that of the G - M tube. In this way too quenching may be carried out electronically as well as internally by means of ethylene.

3. 5. Counter Filling Apparatus.

The apparatus designed for this is shown in fig. 6. The two one-litre storage bulbs were connected to a vertical tube fitted with a number 4 sinter S_1. This tube dipped into mercury contained in a beaker furnished with a small movable tube of the type described previously in section 2. 9. and fig. 2.

FIG. 6.



The bulbs were also connected to the main vacuum line through A, fig. 6 for evacuation. Connection too was arranged through Tap T_1, to a mercury manometer M and cold-finger C, and to the G - M tube by means of a ball and socket joint, J.

3. 6. Counter Filling Procedure.

The G - M tube was attached to the filling apparatus and evacuated carefully to avoid straining the window. Evacuation was carried out by gradually expanding the gas in the G - M tube into the section cut off by tap T_1. The tap on the tube itself was then closed and T_1 opened to the pumps. Tap T_1 was then closed again and a second expansion carried out.

When the whole section, including the G - M tube was evacuated taps T_1 and T_2 were closed and ethylene allowed to expand from its reservoir. The amount could be estimated from the fall in mercury level in tube S fig. 6. Tap T_1 was then opened and ethylene allowed to enter the G - M tube to the required pressure as measured on the manometer.

Tap T_1 was closed again and liquid nitrogen placed around the cold-finger. When the ethylene in the G - M tube side of tap T_1 was condensed, the excess on the other side was pumped away through T_2 and argon, from the other storage bulb, allowed to collect in its place, the amount again being estimated from the fall in mercury

level in tube S.

T_1 was then opened and argon allowed to enter the G - M tube to the required pressure, whereupon tap T_1 was closed and the liquid nitrogen removed. The ethylene evaporated and the mixture was allowed to come to equilibrium for 10 minutes before final adjustments of total pressure were made by expansion to the evacuated side of Tap T_1 .

Tap T_1 was then closed and the G - M tube removed from the section carefully so as not to allow any sudden inrush of air to the filling section. The ball and socket arrangement was particularly convenient for this purpose.

3. 7. Counting Standard.

It was thought desirable to have a radioactive source with which to test the counter characteristics.

Such a source could also be used to compare the count rates observed in one experiment with those observed in another, if after each experiment a count rate was recorded for the standard. For this latter purpose it was necessary to ensure that the counting geometry could be standardised.

A source fulfilling these requirements was produced in the following way. A quantity of lead chloride labelled with chlorine - 36 was precipitated from chlorine - 36 labelled sodium chloride solution by addition of an excess of lead

nitrate solution. The precipitate was centrifuged, taken up as a slurry with alcohol and deposited at the bottom of a tube which had been made from a B - 34 socket.

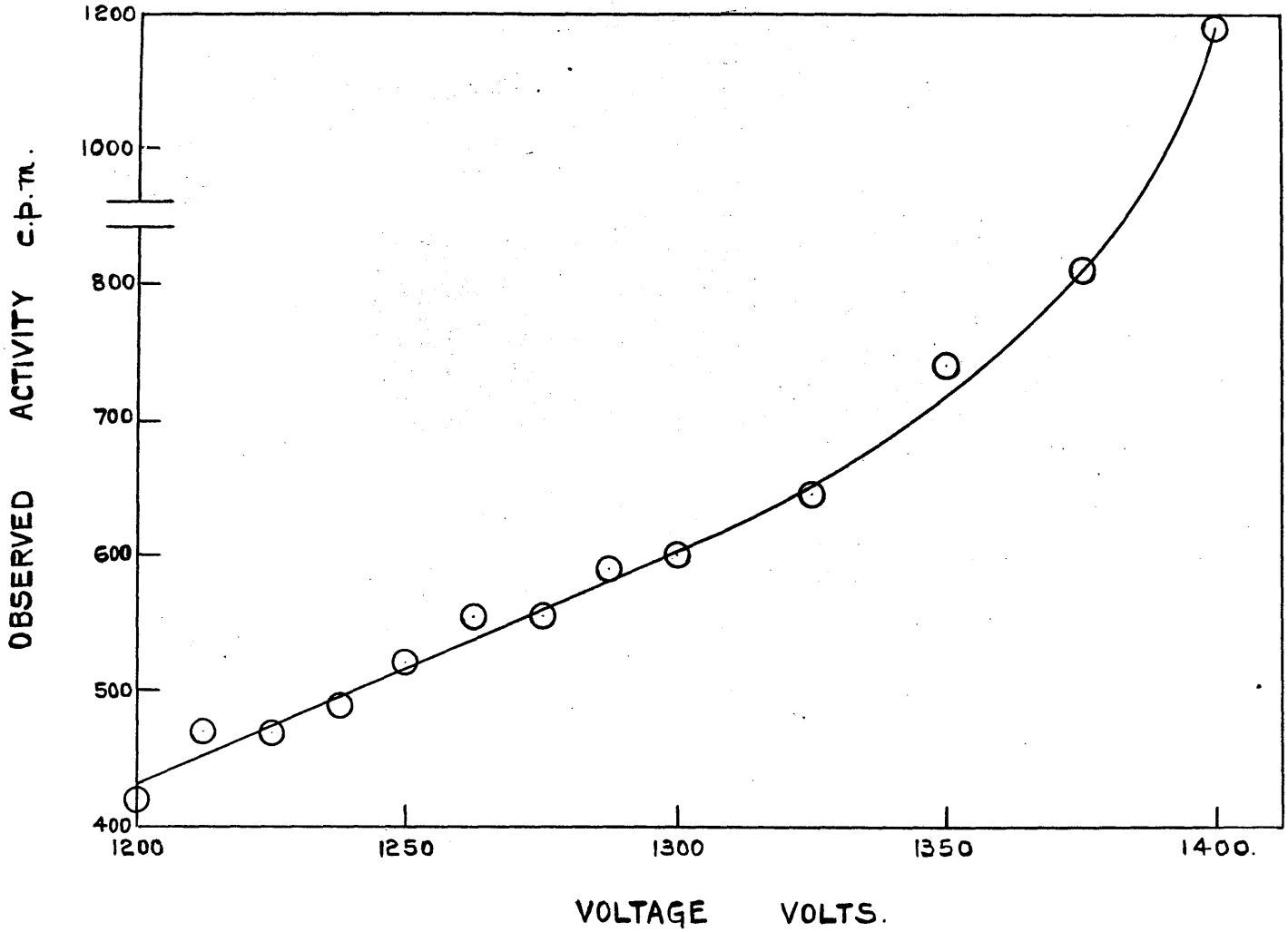
The tube was of a length, such that when the B - 34 cone of the G - M tube was fitted into it, the window came to within 2 cm of the sample. Thus the distance between source and tube window was kept constant. Marks on both tube and counter were brought to coincidence each time to avoid the possibility of altering the geometry of the system by rotation.

3. 8. Counter Filling and Characteristics.

Having obtained a G - M tube embodying the necessary features and having decided to fill it with argon and ethylene the following variables had now to be studied. These were the total pressure of the filling and the partial pressures of the constituents. The objective was the best counting characteristics possible.

To begin with a ratio of partial pressure of ethylene to total pressure of 0.1 was arbitrarily selected and the total pressure varied so as to obtain a long flat 'plateau region' showing low variation in count rate with change in voltage. These results are shown in graphs fig. 7, 8, 9 and are also tabulated, table 1. The slope of the plateau is given as a percentage rise in count rate per 100 V rise in potential applied to the G - M tube.

FIG 7.


1200
1000
800
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600
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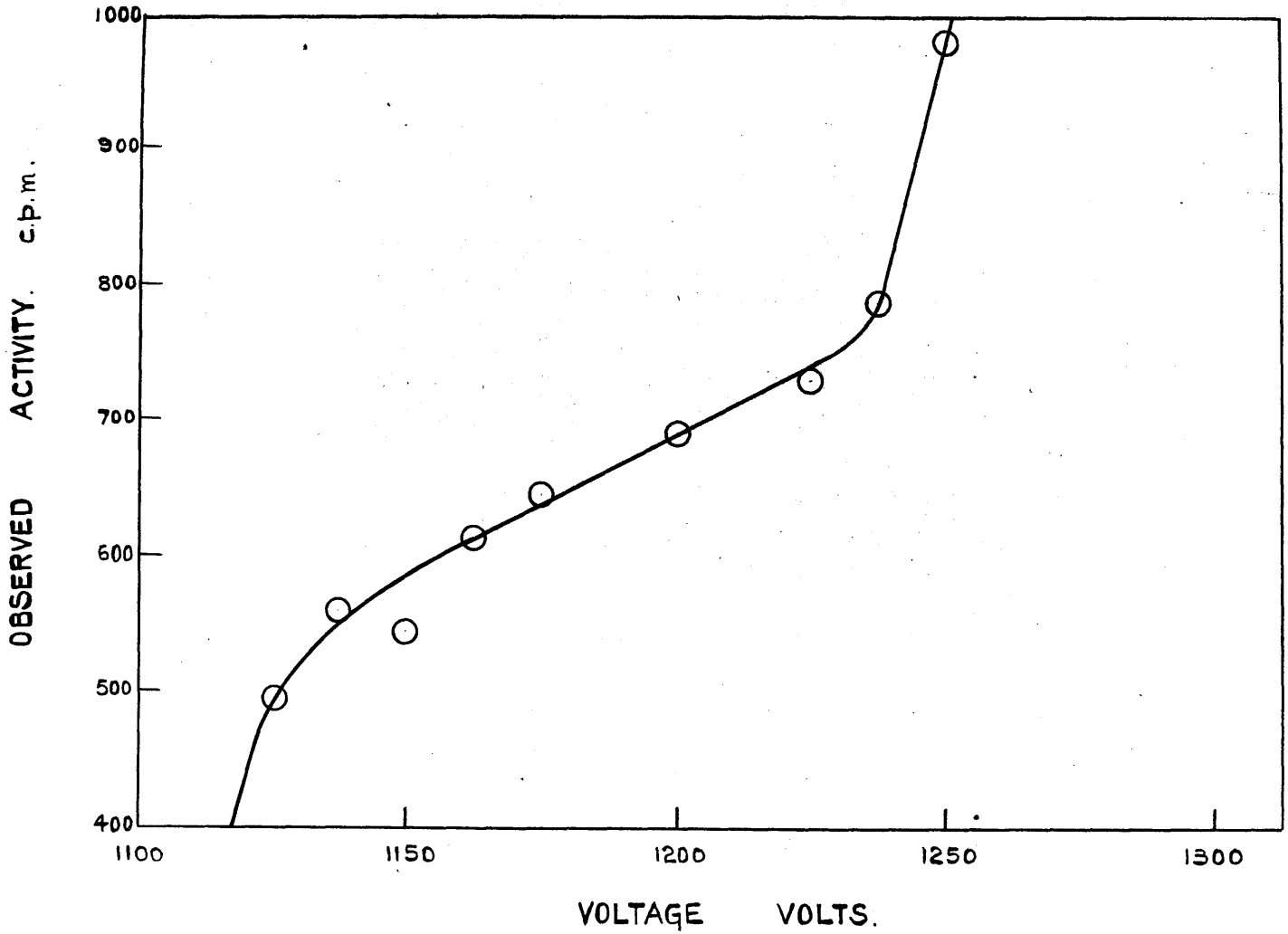
400
OBSERVED ACTIVITY c.p.m.
1200
1250
1300
1350
1400.
VOLTAGE VOLTS.

FIG 8


OBSERVED ACTIVITY. c.p.m.
1000
900
800
700
600
500
400
1100
1150
1200
1250
1300
VOLTAGE VOLTS.

T A B L E 1

COUNTER FILLING SPECIFICATION AND PLATEAU SLOPE

TOTAL PRESSURE	P.P. ETHYLENE/TOTAL PRESSURE	SLOPE
cm		% per 100 V
9	0.1	36
7.5	0.1	36
6.5	0.1	No Plateau

T A B L E 2

COUNTER FILLING SPECIFICATION AND PLATEAU SLOPE

TOTAL PRESSURE	P.P. ETHYLENE/TOTAL PRESSURE	SLOPE
cm		% per 100 V
10	0.05	No Plateau
11.5	0.26	16
12	0.35	4

The characteristic curves for these fillings were quite unsatisfactory.

The ratio of ethylene partial pressure to total pressure was now varied and the results graphed fig. 10, 11, 12 and tabulated, table 2.

Thus a ratio of $\frac{1}{3}$ was adopted for the filling mixture and a total pressure of 12 cm.

3. 9. G - M Tube - Catalyst Holder System.

In the first system the cylindrical counter had been placed axially along the reaction vessel from the end opposite the furnace, being held in place by a B. 34 cone and socket arrangement. The cylindrical catalyst holder with the catalyst adhering to the inside surface could be moved along from the furnace region to surround the G - M tube. In this position a total count representing surface activity plus gas phase activity could be obtained. On slipping the holder back again towards the furnace region the count rate obtained represented gas phase activity only. In this way the surface activity could be determined.

As pointed out earlier it is important to ensure that the holder always returns to the same position relative to the G - M tube. This was achieved by tilting the reaction vessel to such an extent each time that the holder slides firmly against the B. 34 cone with which the G - M tube is fixed into the end of the reaction vessel.

FIG 10

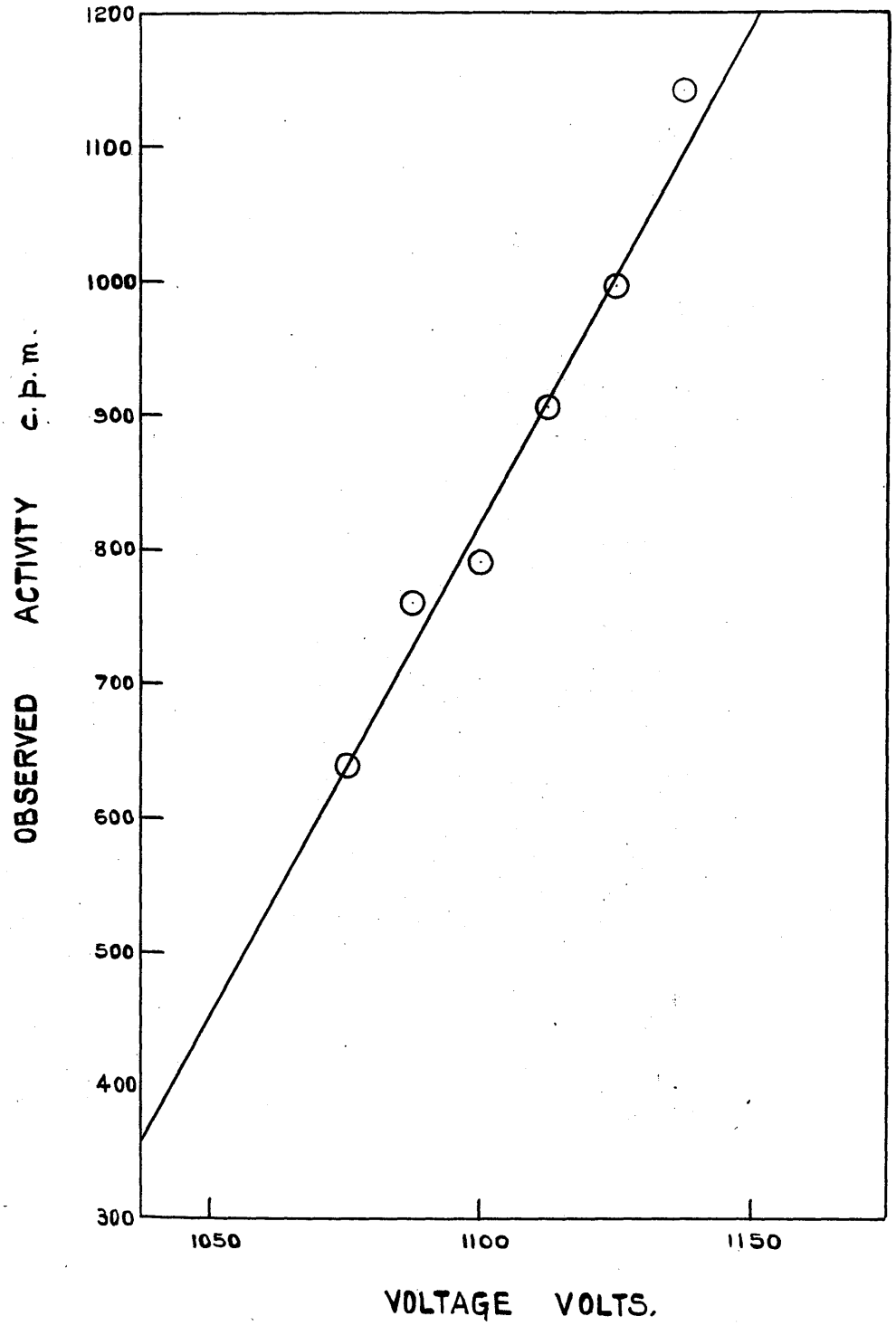

1200
1100
1000
900
800
700
600
500
400
300
OBSERVED ACTIVITY c. p. m.
1050
1100
1150
VOLTAGE VOLTS.

FIG. 11.

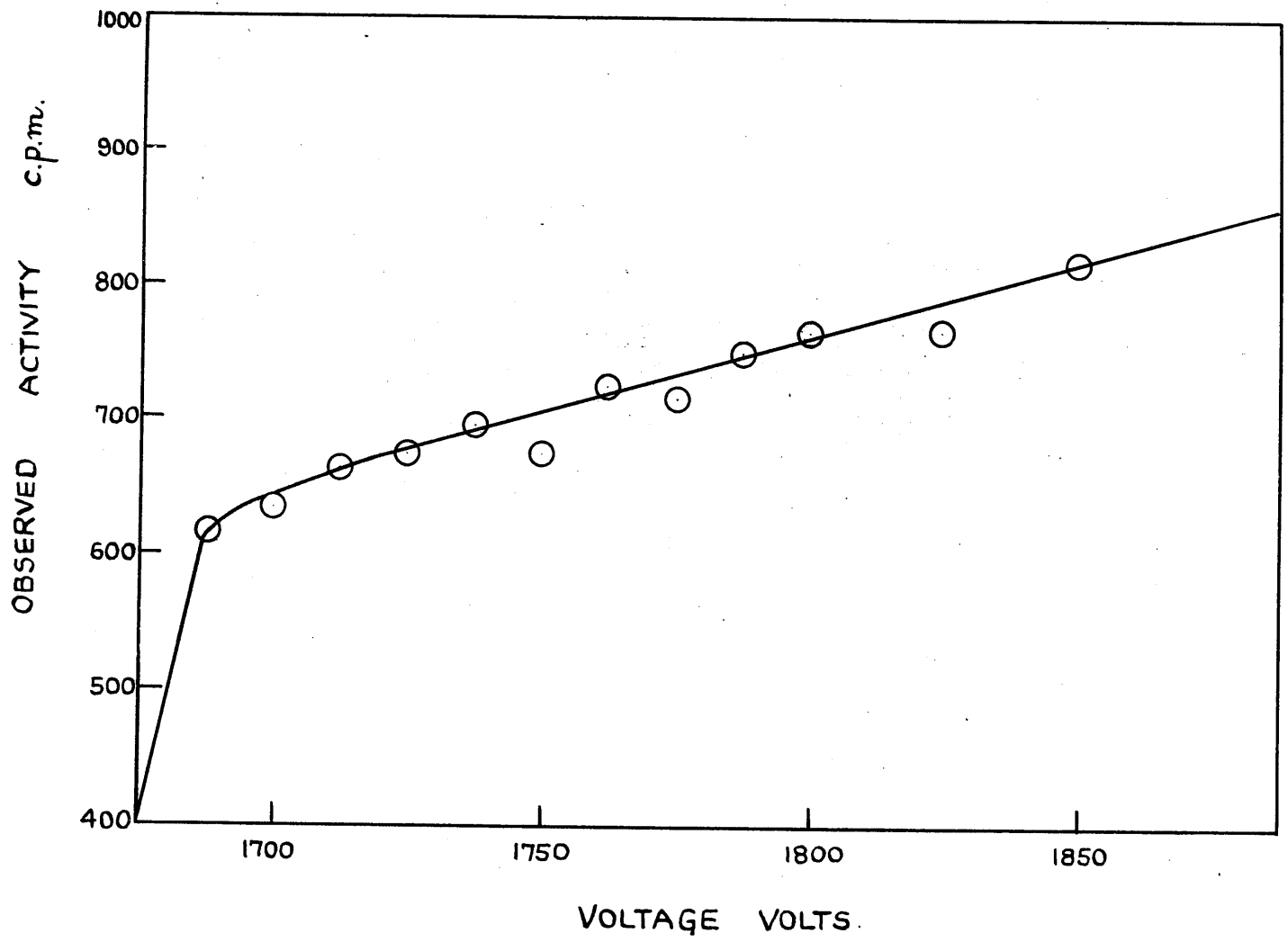
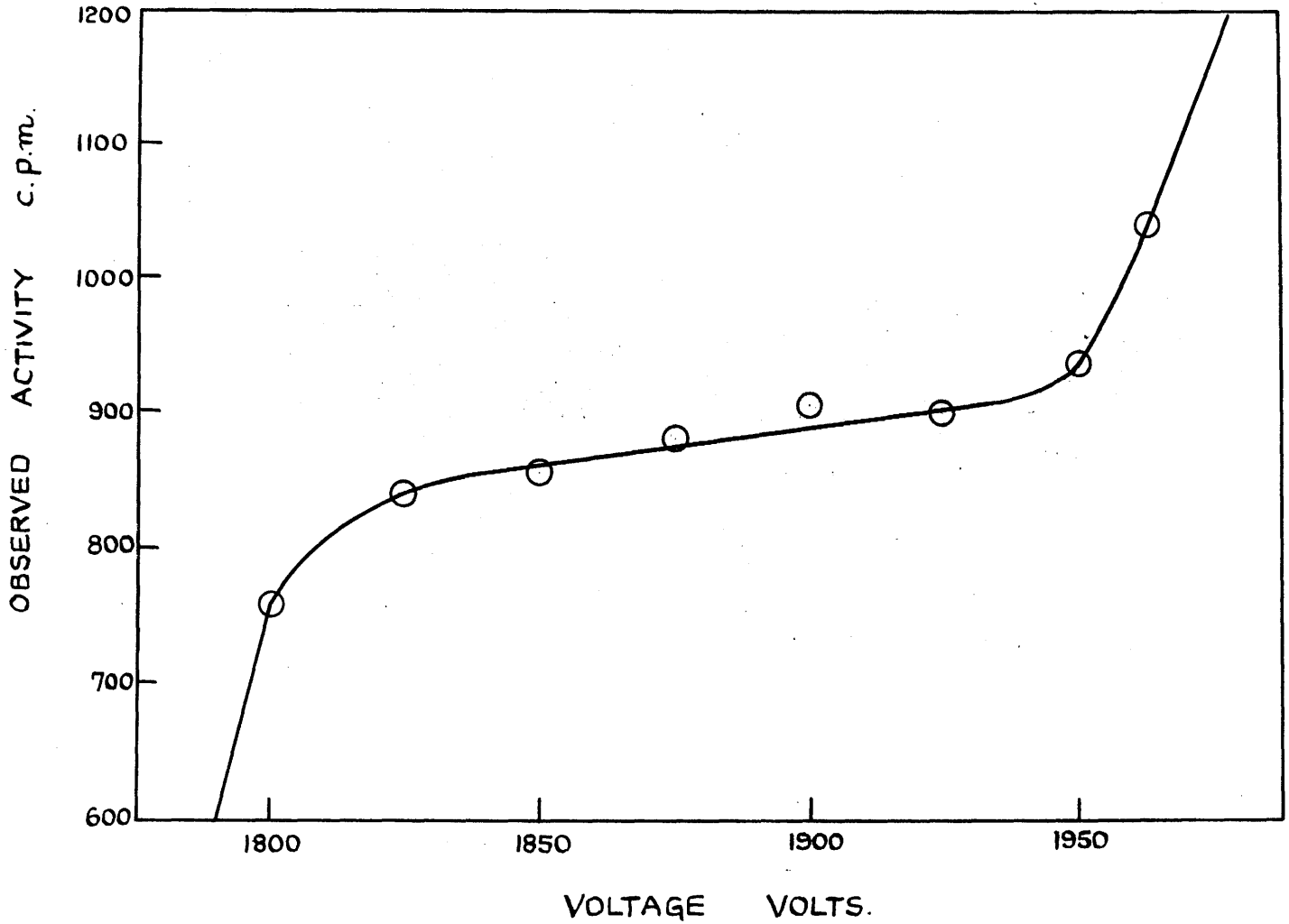

1000
900
800
700
600
500
400
OBSERVED ACTIVITY c.p.m.
1700
1750
1800
1850
VOLTAGE VOLTS.

FIG. 12.


1200
1100
1000
900
800
700
600
OBSERVED ACTIVITY c.p.m.
1800
1850
1900
1950
VOLTAGE VOLTS.

However owing to the method of construction of the G - M tube a further point had to be considered. Because of the soldered seam in the copper cathode and the Araldite seam in the Mellinex film the β-particle transparency is not constant over the entire surface of the G - M tube. This fact together with the impossibility of spreading the catalyst in a completely uniform film forces a consideration of the possibility of rotation of the catalyst holder.

However this difficulty was avoided when the end-window G - M tube was adopted. A cylindrical holder which slid over the G - M tube until it made contact with the B. - 34 cone was used as before. This time however one end of the cylinder was closed. With the holder in the monitoring position the closed end was 5 cm from the window of the G - M tube. The Catalyst was caused to adhere to the inside surface of this closed end of the cylinder. Thus in this arrangement the catalyst surface was always brought to the same distance from the G - M tube window and rotation of the holder made little difference to the observed count rate.

This change however led to difficulties in computing the surface activity in the catalyst at any time. Although the surface count rate could be reduced to zero by moving the holder far enough away from the window, the gas phase activity

observed in this position, 'infinite distance' was not the gas phase activity observed when the holder was close up to the window.

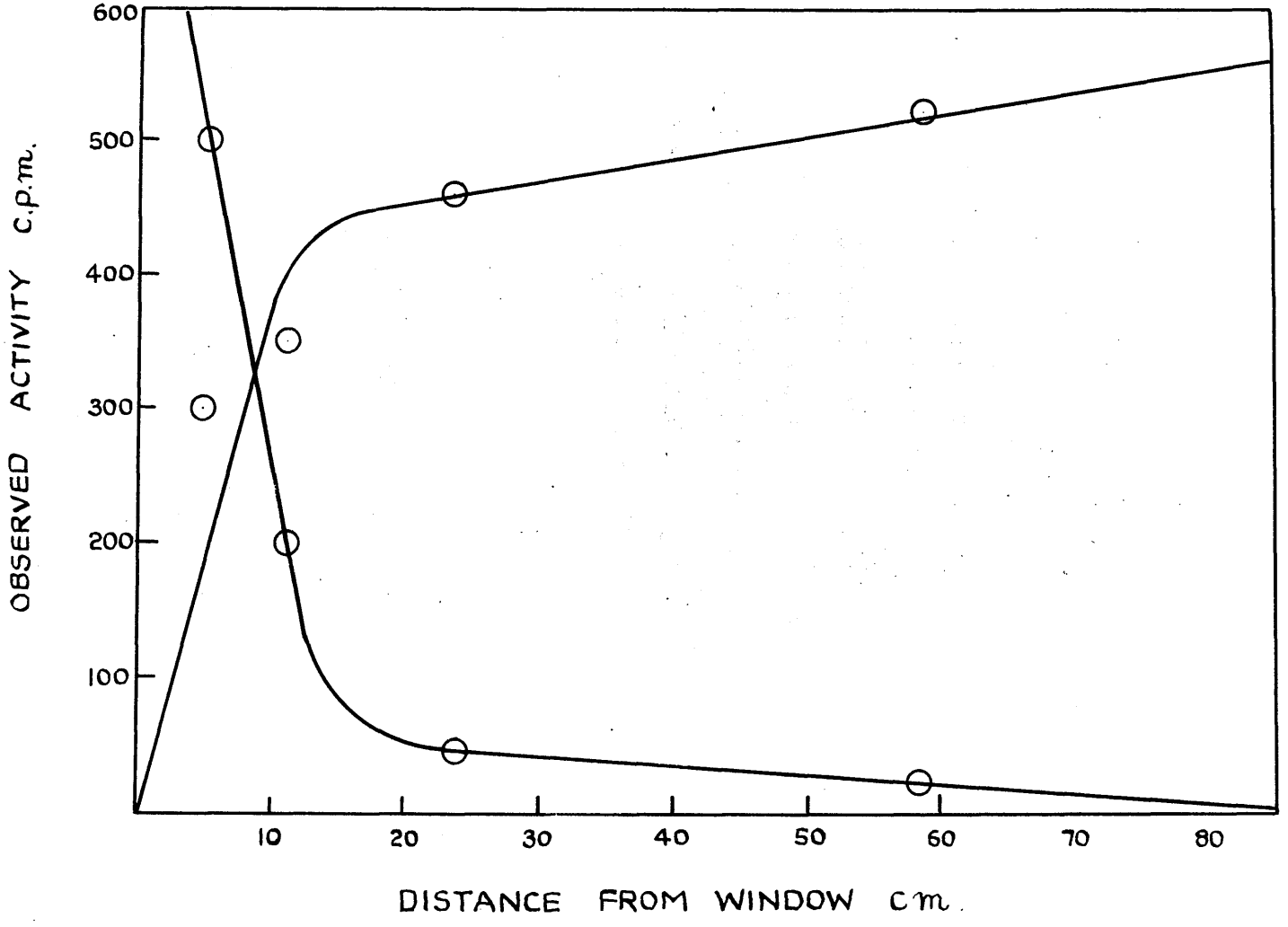
Thus before the system could be used, standard curves had to be obtained showing the effect of removing the catalyst holder on both the surface and gas phase count rates independently.

By admitting ethylene - C - 14 to a rhodium catalyst and then pumping away the gas it was discovered that some of the ethylene remained adsorbed. This radioactive catalyst sample was then placed at varying distances from the G - M tube window in the reaction vessel and count rates taken. The graph of count rate against distance for this surface activity is shown in fig. 13.

A blank experiment was then carried out in which gas phase count rates were obtained for different positions of the empty catalyst holder. The graph of these results is also shown in fig. 13.

Although this method was later discarded it was proposed to use these curves in the following way. After a total count had been taken the holder was to be moved to 'infinite distance' thereby reducing the surface count to zero and enabling the gas count at 'infinite distance' to be measured. Using the gas phase standard curve the gas count with

FIG. 13.


600
500
400
300
200
100
OBSERVED ACTIVITY c.p.m.
10
20
30
40
50
60
70
80
DISTANCE FROM WINDOW cm.

the holder in the position for total count could be computed. This value could then be subtracted from the total count to give the surface count.

This proposal however raised a certain question which had to be answered experimentally. What effect does the change of pressure resulting from the hydrogenation of ethylene in a given experiment have on the gas count observed at 'infinite distance'?

To answer this, the following experiment was carried out. A quantity of ethylene - C - 14 was admitted to the reaction vessel and gas phase count rates obtained for different positions of the empty catalyst holder. An equimolar mixture of hydrogen and ethylene was now admitted to the reaction vessel to give a pressure of 6.7 cm. Count rates were again observed for different positions of the holder. The graphs are shown in fig. 14. The presence of the hydrogen-ethylene mixture at this pressure caused a 10.4% decrease in count rate at 'infinite distance'. This experiment was repeated, fig. 15. This time a reduction of 8.4% was observed in the count rate at 'infinite distance' for a mixture pressure of 5.5 cm.

The gas phase count rate is therefore seen to depend on the pressure of the hydrogen-ethylene mixture present.

FIG. 14.

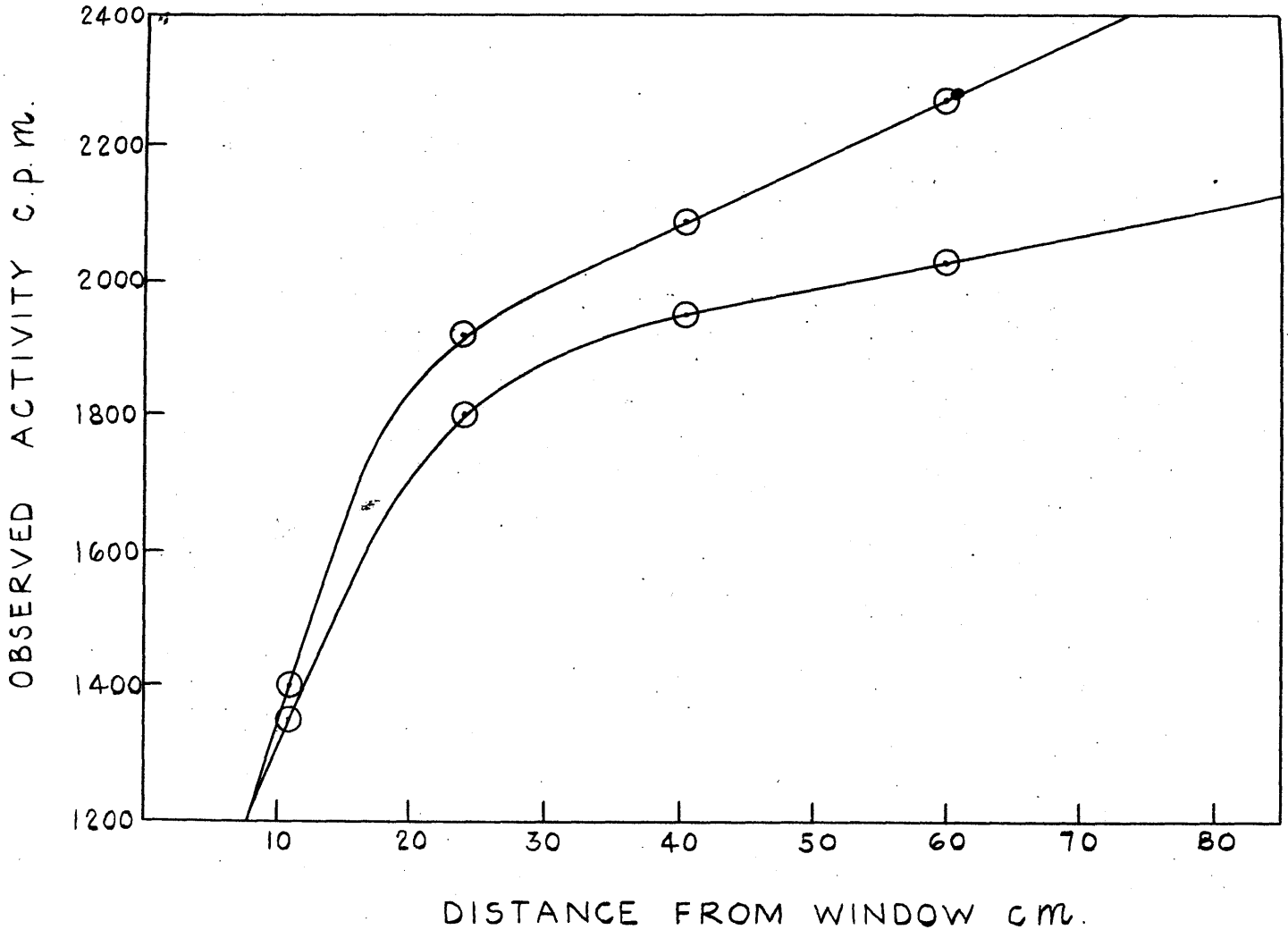
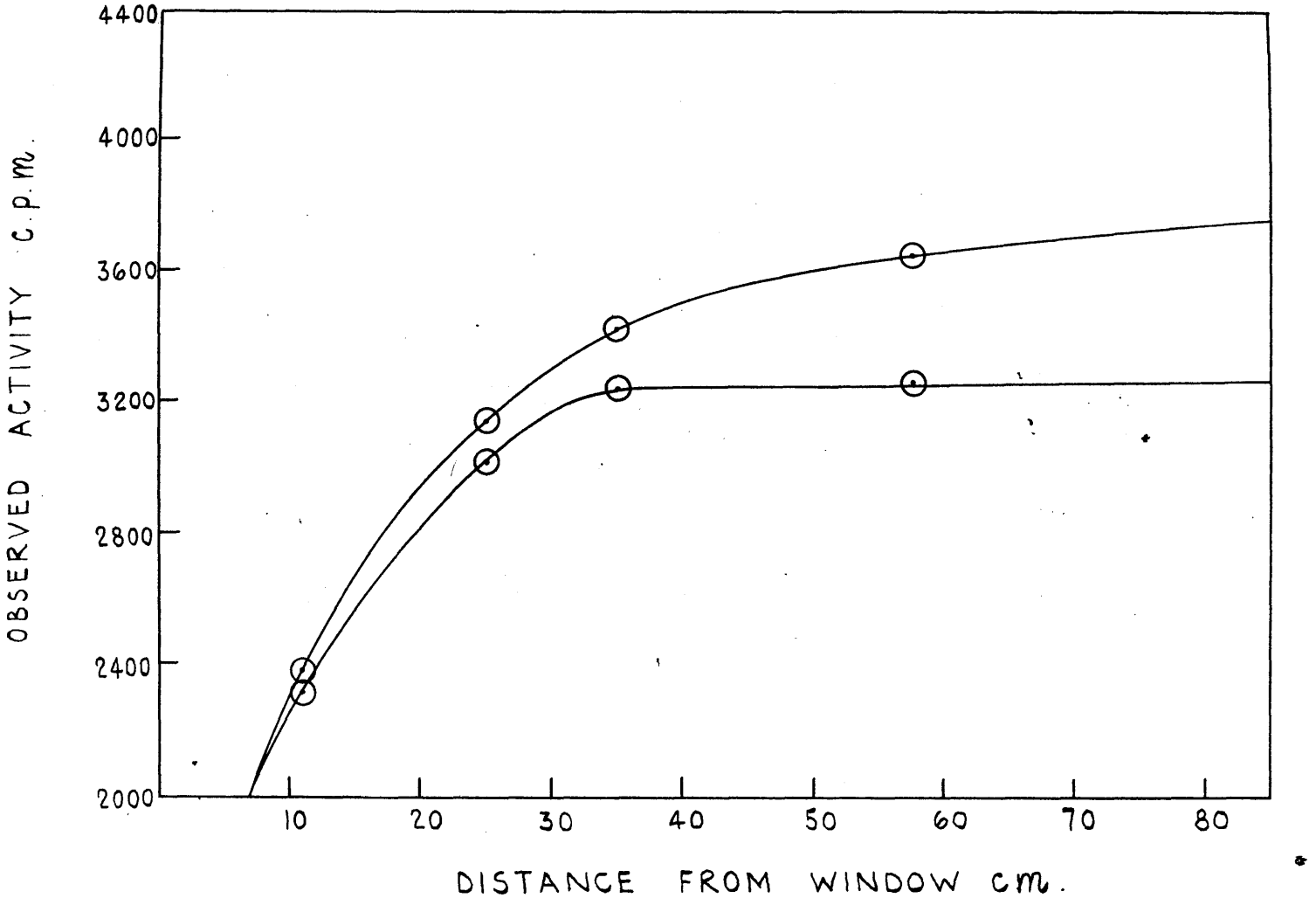

2400
2200
2000
1800
1600
1400
1200
OBSERVED ACTIVITY c.p.m.
10
20
30
40
50
60
70
80
DISTANCE FROM WINDOW cm.

FIG. 15.


4400
4000
3600
3200
2800
2400
2000
OBSERVED ACTIVITY c.p.m.
10
20
30
40
50
60
70
80
DISTANCE FROM WINDOW cm.

These results could have been used in drawing up another standardisation curve. However it was felt at this stage that what was meant to be a method of direct observation of surface activity was ceasing to be in any way direct. Accordingly it was decided to make a new approach to the problem.

3. 10. Final G - M Tube - Catalyst Holder System.

The difficulties of interpretation referred to in the previous section arose from the axial position of the end-window counter derived from the axial position of the original cylindrical counter. It now appeared that a reasonable change would be to place the G - M tube at right angles to the axis of the reaction vessel and to use a hemi-cylindrical catalyst holder which could be moved parallel to the axis of the catalyst vessel. In this way the gas phase activity could be made the same in both the counting positions of the holder.

In order to improve the constancy of the gas phase count rate in both counting positions the holder was made longer than required to spread the amount of catalyst used. In fact catalyst was spread over only half the holder at most. Thus when the gas phase count was to be taken the holder was not removed completely from under the G - M tube window but only that part to which the catalyst adhered. The volume of gas 'seen' by the counter remained the same and did not increase as it

would have done had the holder been removed entirely.

It was ensured that the holder came firmly against the end of the catalyst vessel before a total count was taken. In this way the holder was always returned to the same position after a blank or gas phase count had been taken. As far as rotation of the holder was concerned too dimples were put in the walls of the reaction vessel to guide the holder in its longitudinal motion and to prevent one side rising or falling with respect to the other.

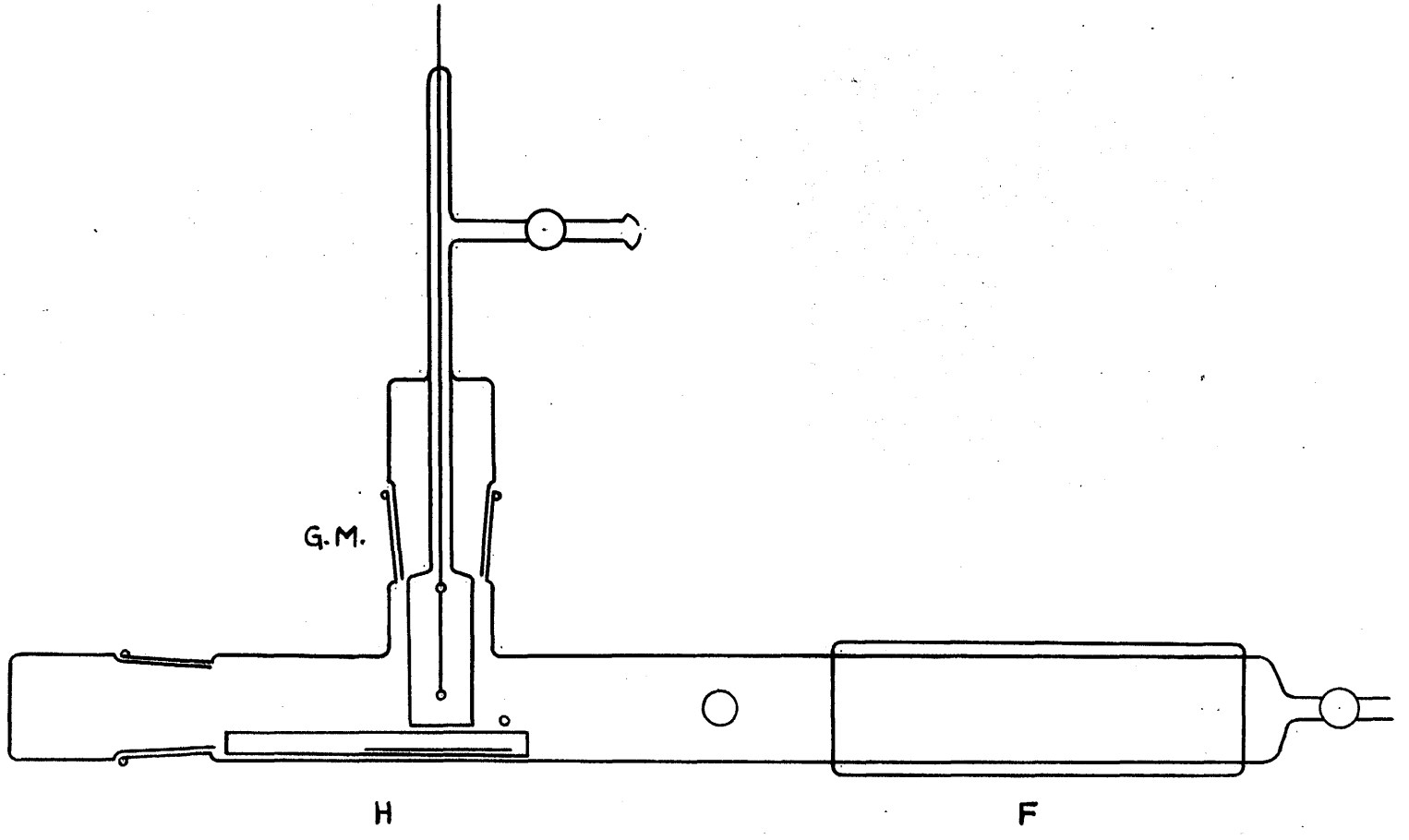
By these means then constant counting geometry was maintained. The final arrangement is shown in fig. 16.

The catalyst holder H with catalyst spread over half its length, is shown under the counter G - M. The furnace F is placed at the opposite end of the reaction vessel.

3. 11. Discussion of the G - M tube-catalyst Holder System.

The question raised by the previous system concerning the effect of pressure change on the gas phase count arises here also. However the distance between the G - M tube window andthe catalyst surface is now only 2 cm. Fig. 14, 15, show that the reduction in count rate brought about by addition of hydrogen ethylene mixtures decreased as the holder is brought closer to the G - M tube window and is negligible at a distance of 2 cm. Thus this effect can be ignored in the

FIG. 16.



present system.

To confirm this the following experiment was carried out. A quantity of ethylene - C - 14 was introduced to the reaction vessel followed by an ethylene-hydrogen mixture. A count rate was taken. Some of the gas was then pumped away to reduce the pressure and a second count taken. This process was repeated several times. A graph of count rate against pressure is shown in fig. 17. Linearity here shows that overall pressure is not affecting the ability of the G - M tube to record the activity in the gas phase. The result of a second experiment on the same lines is shown in fig. 18.

There is a second possibility viz that a given surface activity may give rise to different count rates depending on gas pressure between the catalyst surface and the G - M tube window.

This was tested by placing a counting standard of polymethylmethacrylate - C - 14 in the catalyst holder and observing the count rate obtained with varying gas pressure. Any such effect was found to be negligible.

At this point it was concluded that a reasonable experimental system had been developed, one which allowed direct measurements to be taken of surface activity, one in fact which enabled us to solve the problem as set out in Chapter I.

FIG. 17.

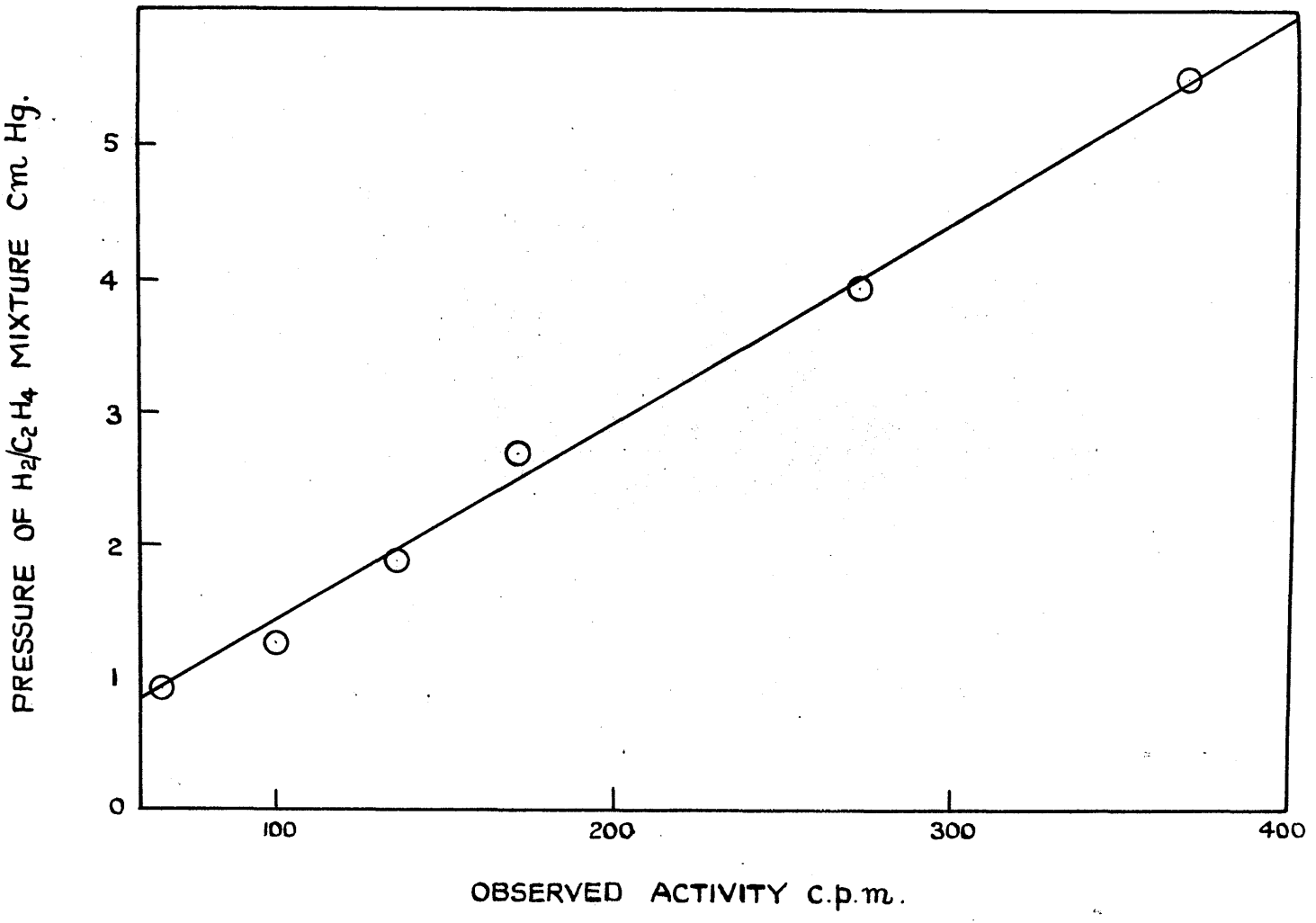
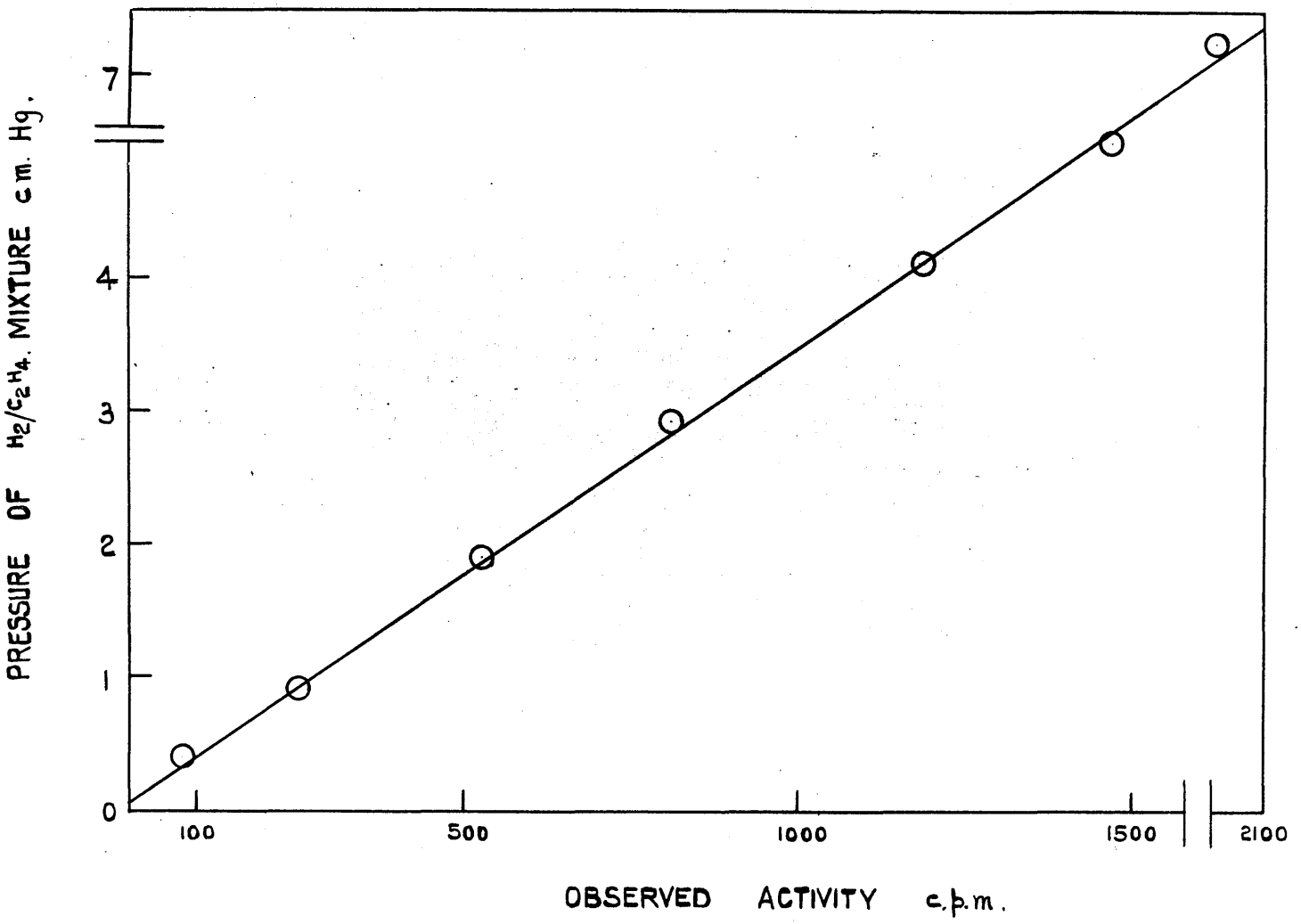

PRESSURE OF H_2/C_2H_4 MIXTURE Cm. Hg.
0
1
2
3
4
5
100
200
300
400
OBSERVED ACTIVITY c.p.m.

FIG. 18.


PRESSURE OF H_2/C_2H_4 MIXTURE cm. Hg.
0
1
2
3
4
7
100
500
1000
1500
2100
OBSERVED ACTIVITY c.p.m.

CHAPTER 4

EXPERIMENTAL PROCEDURE AND RESULTS

4. 1. Introduction

The aim was to measure the amount of primarily adsorbed ethylene - C - 14 retained by the catalyst after reactions involving this ethylene had taken place, and to express this as a percentage of the primary adsorption. It was therefore necessary to ensure complete saturation of the catalyst initially. This was done by obtaining an adsorption isotherm and continuing the measurements until saturation was observed.

On admitting a reaction mixture of hydrogen and non-radioactive ethylene, the change in the total count rate was observed until a constant value was reached. At this point the activity of the surface was measured. This activity represented the extent to which the initially adsorbed ethylene - C - 14 had been retained.

If instead of hydrogen and non-radioactive ethylene, a quantity of the latter alone, was admitted, the extent of retention after ethylene molecular exchange between surface and gas phase was obtained.

Following on this, the effects on the retained activity of treatment with hydrogen and of evacuation were observed.

4. 2. Apparatus

This section deals with those components of the apparatus actually used in making the measurements required. Fig. 19 shows the arrangement of this apparatus.

It consisted of the reaction vessel, B.34 cone and socket at one end and tap T_6 at the other, placed horizontally in front of the other components and fitted with the G - M tube G. M. and furnace F.

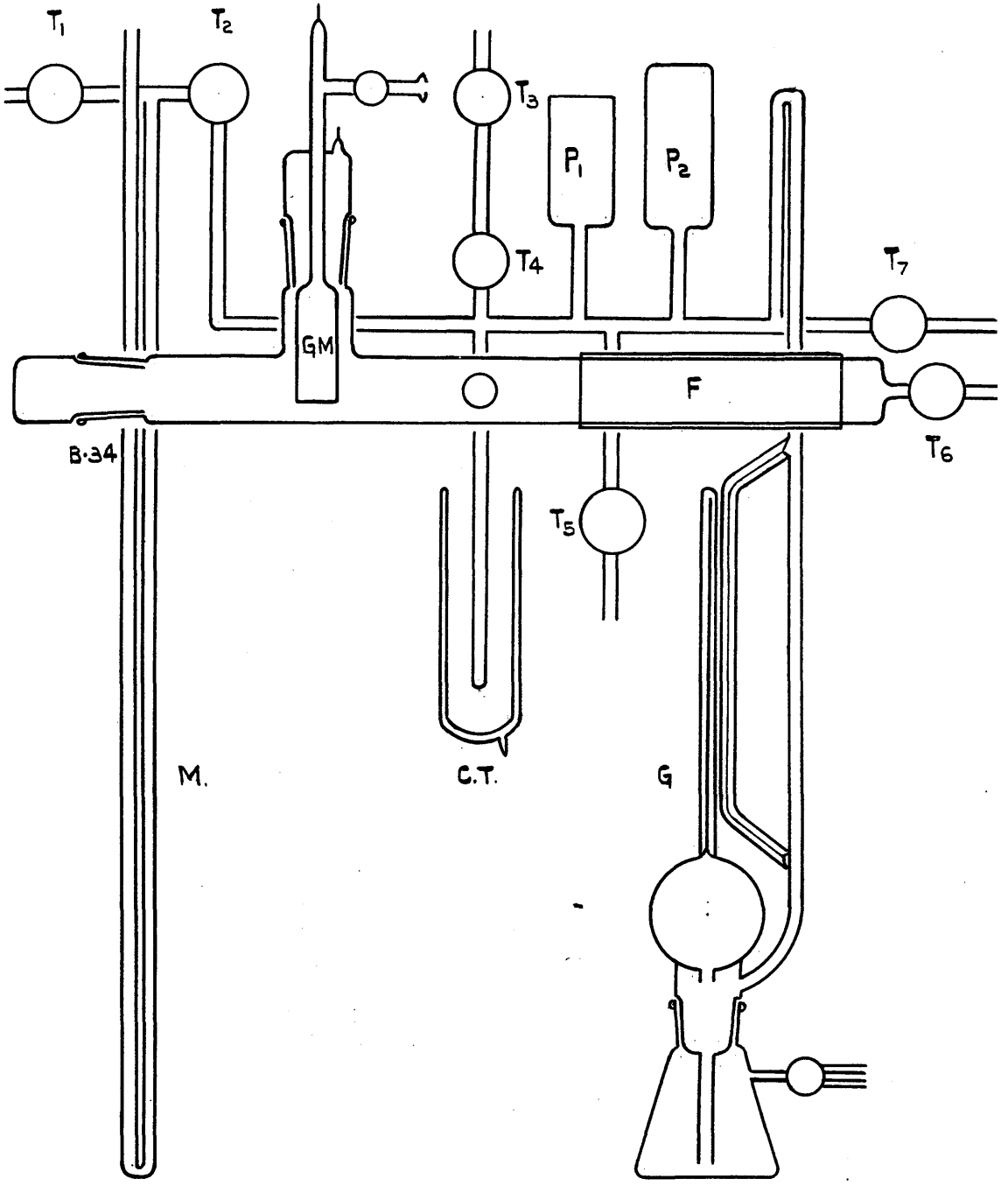
Measuring devices were connected to the reaction vessel via the cold trap C. T. They were the mercury manometer M, Pirani gauge P_1, Penning gauge P_2 and the McLeod gauge G.

The reaction vessel could be connected to the atmosphere through the cold trap and tap T_5.

The apparatus described above was connected to other components, not shown in fig. 19 in the following way. Tap T_1 connected it with the reactant mixing flask M, fig. 3 which in turn was joined to the reservoirs containing hydrogen and ethylene. The ethylene - C - 14 supply was connected to the reaction vessel through taps T_3 and T_4, fig. 19 and the mercury cut-off valve, fig. 3.

The entire section shown in fig. 19 could be evacuated through tap T_7.

FIG 19.



4. 3. Procedure.

It is proposed here to take one catalyst as an example and to describe the sequence of operations necessary to obtain the desired results.

First of all one has to discover the quantity of catalyst necessary to give a conveniently measurable reaction rate and which was capable of being saturated with a reasonable quantity of ethylene - C - 14. When this had been discovered from preliminary studies, such a quantity of catalyst, 67 mg in the case of palladium, was weighed out, mixed with about $\frac{1}{3}$ of its weight of the montmorillonite preparation and spread evenly as a slurry with water over half the length of the catalyst holder. This was dried out in an oven at 100° C and placed in the furnace region of the reaction vessel.

The behaviour of the G - M tube was now checked by counting the external chlorine - 36 standard and obtaining a characteristic curve. If the plateau was not satisfactory the tube was refilled. A plateau slope greater than 5% per 100 V was taken to be unsatisfactory. The G - M tube, in a working condition was then inserted in the reaction vessel as shown, fig. 16, 19.

Hydrogen was then passed over the catalyst for six hours by connecting T_5 to a hydrogen supply cylinder. Tap T_6 was opened to a bubbler so that the flow of hydrogen through the reaction vessel

could be checked at a glance. The effluent hydrogen was finally drawn through the laboratory exhaust system. The furnace was switched on during this time giving an internal temperature of 500° C.

The hydrogen was switched off after six hours and taps T_5 and T_6 were closed. The reaction vessel was then evacuated through tap T_7 and pumping continued for a further six hours at 500° C to outgas the catalyst. The furnace was then switched off and pumping continued overnight.

Next morning the vacuum was checked, formerly with the Pirani and Penning gauges, but now with the McLeod gauge also, this being a later addition to the system. Pressures measured at this stage were of the order of 10^{-4} mm.

To prevent entry of mercury vapour to the reaction vessel an ethanol - liquid nitrogen cold trap was now prepared for use in position C.T. fig. 19. This is best done by keeping the two components separate in the following way. Liquid nitrogen was poured into a boiling tube which was surrounded by ethanol contained in a Dewar flask. By repeated filling of the boiling tube the temperature of the ethanol in the Dewar flask can be reduced to - 125° C. Normally however a temperature of -70° to -90° C was maintained during an experiment.

A small quantity of ethylene - C - 14 was now allowed to enter the reaction vessel. On moving the catalyst under the

G - M tube by rotating the reaction vessel, a count rate could be obtained which was the sum of contributions from the adsorbed material and from the gas phase between the surface and the G - M tube window. The gas phase contribution alone was then obtained by slipping the catalyst from under the window so that the counter "saw" only the empty region or the holder from which there is no count plus the gas phase count. This was then subtracted from the total. This process, consisting of the admission of ethylene - C - 14 to the reaction vessel followed by two activity measurements, was repeated until no increase in surface activity was observed for subsequent admissions of ethylene - C - 14.

The results for such an adsorption isotherm determination are tabulated, table 3 and a graph drawn, fig. 20. On incorporating a McLeod gauge the pressure of the ambient gas at saturation was found to be 5.9×10^{-2} mm in the case of palladium.

Having obtained saturation of the catalyst an equimolar mixture of hydrogen and ethylene was now prepared as described in section 2. 10. using manometer M for pressure measurements, tap T_2 being closed.

This equimolar mixture was then admitted to the reaction vessel through tap T_2 and total count rates taken every alternate minute until constant count rate was obtained. These results for palladium are shown in fig. 21 and table 4. During this time the course of

hydrogenation was followed by observing pressure changes with the manometer M, tap T_1 being closed. The results are shown in fig.22 and table 4.

When no further change in total count rate was observed the catalyst was removed from under the counter and the gas phase activity obtained. If no change could be found in the gas phase activity with time it was subtracted from the total activity to give the surface activity. Thus we have the percentage of initially adsorbed ethylene which cannot be reacted from the surface. In the case we are now considering it was found to be 70%, table 6.

The gases in equilibrium with the surface were now pumped away and more ethylene - C - 14 admitted to the reaction vessel in order to study the exchange between adsorbed and gas phase ethylene. It was not thoughtnecessary to saturate the surface again however and the surface activity was merely increased beyond the level reached after the ethylene hydrogenation reaction was complete. In this case it was increased to 4157 c.p.m. as opposed to the retained activity of 3758 c.p.m.

Non-radioactive ethylene was now admitted to the reaction vessel and total counts taken against time as before. Finally the retained activity was obtained also as described above. The results are shown in table 5 and graphed in fig. 23.

The ethylene now over the surface was pumped away and the effect of hydrogen on the retained activity was observed. This had the result of reducing the retention to 63% of the original surface

activity.

The percentage retention figures are summarised in table 6.

All the measurements described above and in the following section were carried out at room temperature, 20°C.

4. 4. Discussion

The shapes of the total activity-time curves for both hydrogenation fig. 21 and exchange, fig. 23 require comment.

The removal of pre-adsorbed ethylene - C - 14 from the catalyst surface should result in a decrease in surface activity with time. The activity thus removed to the gas phase should increase the gas phase count. However this increase ought to be less than the decrease in surface count because of the dilution effect brought about by the large volume of the reaction vessel. Thus a decrease in total activity with time is to be expected in this system.

Both curves referred to above show an increase in total activity with time. This is thought to be due to the effect of the non-equilibrium mixing conditions in the gas phase resulting from the admission of hydrogen and ethylene at 10 cm pressure to a system containing gas at a pressure of the order of 10^{-2} mm. Thus the initial gas phase activity was swept away by the incoming ethylene - hydrogen mixture and the subsequent mixing process gave rise to an increase in gas phase activity with time. The competing process, tending to reduce the total activity with time, viz the

removal of activity from the surface to the gas phase is in this case more than cancelled out by the former effect.

In general we may now expect toal activity-time curves to rise, fall or even remain constant, depending on the relative importance of the two effects in any given case.

In the case of palladium where the decrease in surface activity is small the overall effect depends on the return of activity to the monitored region by the mixing process and so an increase in total activity with time is observed. However with catalysts which give low retention of ethylene the total activity-time curve may be expected to show a decrease since here the decrease in activity brought about by removal from the surface may well be paramount. This expectation was fulfilled in the case of platinum where the retention is very low as compared with palladium.

Once constancy in total activity was reached however the expected situation was observed in all cases viz that the total activity had indeed decreased as had the surface activity and the gas phase activity had risen.

The unexpected and varied shapes of the total activity-time curves are therefore unimportant though the curves themselves are. They must be determined in each case to observe when constancy is reached for only then can the final surface activity be determined.

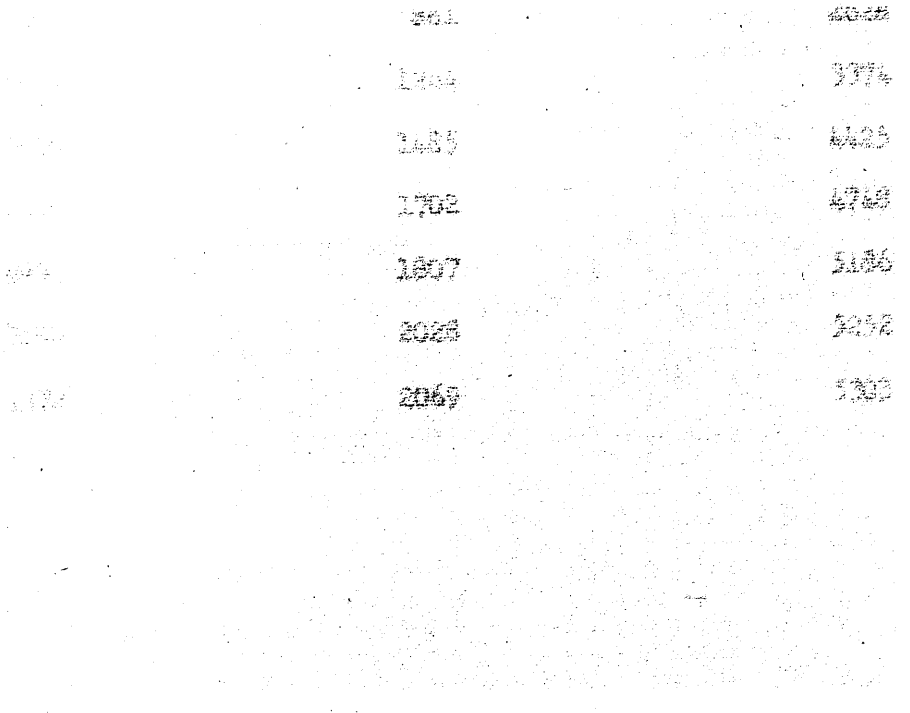
4. 5. Presentation of Results.

The results presented here, in tables and graphs were obtained by following the procedures described in the section 4. 3. They are the results of studying 5% preparations of the metals, nickel, rhodium, palladium iridium and platinum supported on alumina.

A sub-section has been allotted to each of these catalysts. These sub-sections commence with adsorption isotherm data showing saturation of the catalyst in question. This is followed by tables and graphs showing total count variation with time for ethylene hydrogenation and ethylene exchange. These data enable the percentage retention to be computed, if taken in conjunction with gas phase count rates as described previously. Observations were made in all cases of the effect of treatment with hydrogen and of pumping on the retained activity. The last table in each sub-section summarises the retention values for hydrogenation and exchange and also shows the retention values after treatment with hydrogen and after pumping. The so-called gas phase activity after evacuation is in fact the background activity.

No count rate has been used in computing percentage retention without being averaged over at least 5,000 counts. The statistical error on a count of N events is $\pm\sqrt{N}$. Since the count rates used in the computation are the result of a difference between two others they are all effectively corrected for background activity.

All count rates in graphs and tables are as observed, with the exception of the "saturation activity" value shown in the last table of each sub-section. This has been corrected for dead-time losses. The "final activities" shown in these tables were corrected for dead-time losses before the percentage retention figures were computed.



4. 6. Results for palladium catalyst.

T A B L E 3

ADSORPTION ISOTHERM

67 mg 5% PALLADIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1868	.621	1247
3489	861	2628
4638	1264	3374
5910	1485	4425
6450	1702	4748
6993	1807	5186
7280	2028	5252
7372	2069	5303

FIG. 20.

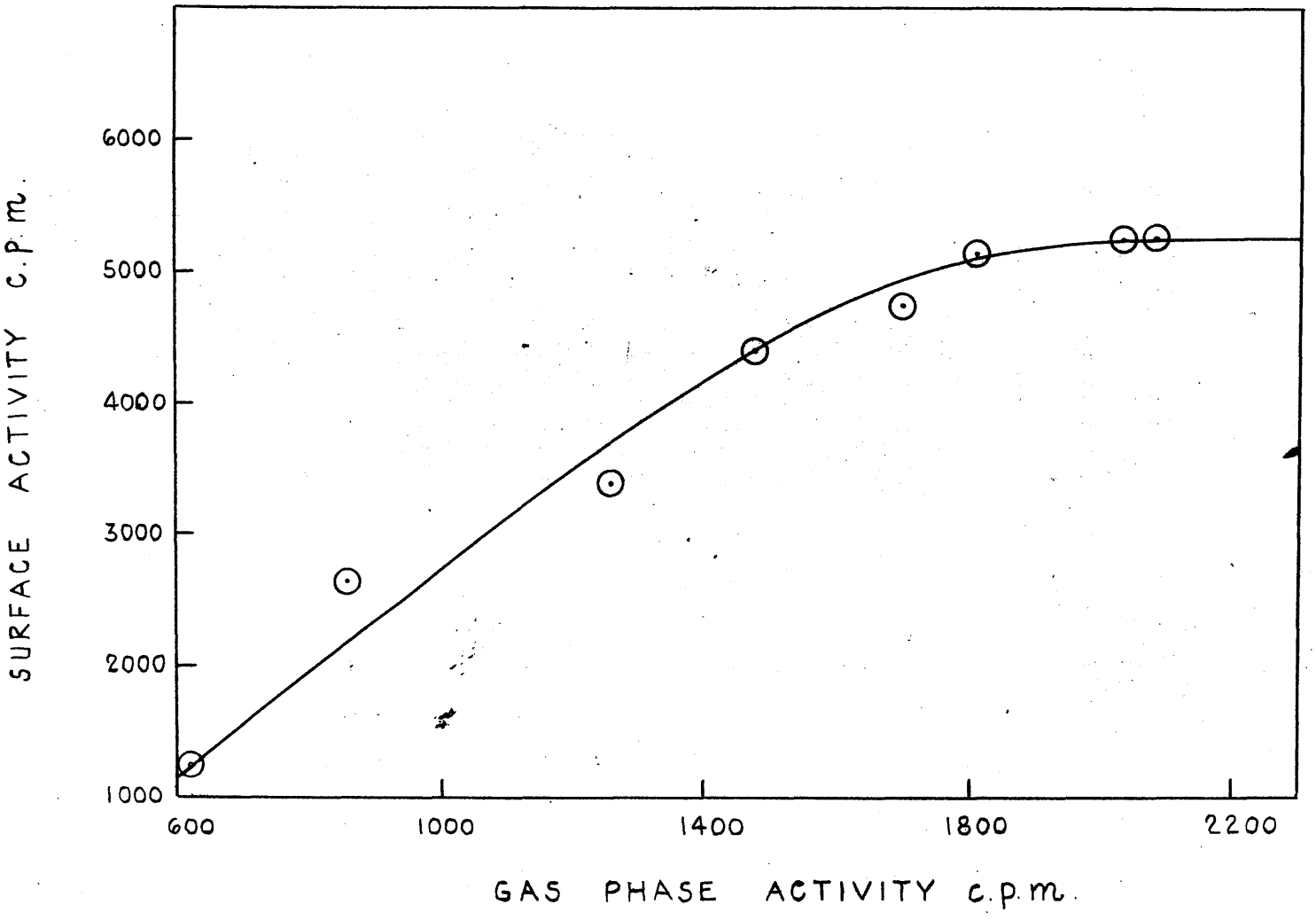

SURFACE ACTIVITY c.p.m.
6000
5000
4000
3000
2000
1000
600
1000
1400
1800
2200
GAS PHASE ACTIVITY c.p.m.

TABLE 4

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

67 mg 5% PALLADIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg.
0	5723	44.4 - 34.8 = 9.6
2	5885	
4	5729	
6	5846	
8	5885	
10	5837	44.2 - 35.0 = 9.2
12	5815	
14	5821	
16	5939	
18	6014	
20	5940	44.1 - 35.1 = 9.1
22	5974	
24	5884	
26	5947	
30	5954	44.0 - 35.3 = 8.7

T A B L E 4 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg.
32	5899	
34	5907	
36	6160	
38	6139	
40	6088	43.8 - 35.5 = 8.3
42	5916	
44	6029	
46	5892	
48	5979	
50	5968	43.6 - 35.7 = 7.9
54	6128	
56	5991	
58	5934	
60	6034	43.5 - 35.8 = 7.7
110	5985	42.7 - 36.6 = 6.1

FIG. 21.

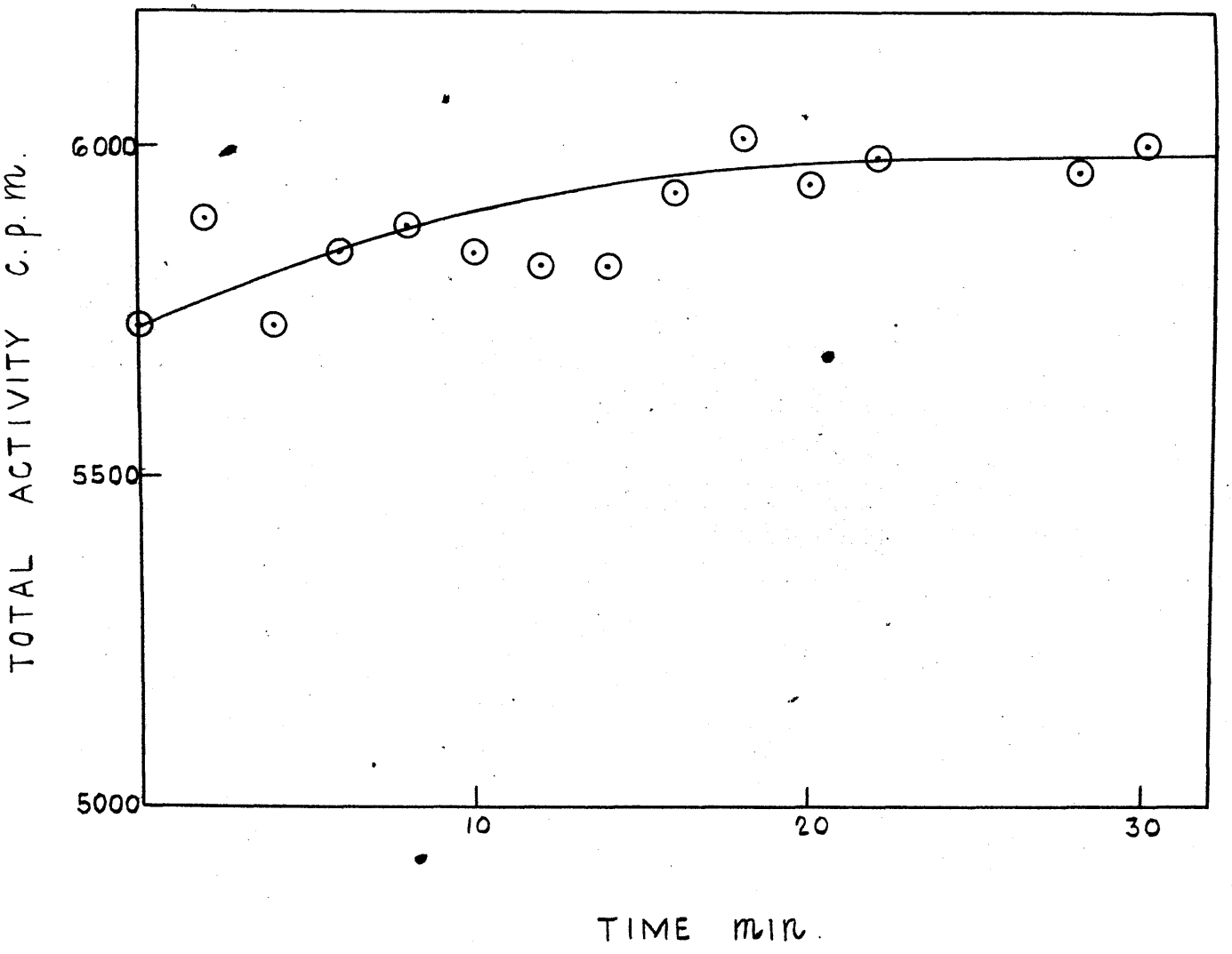
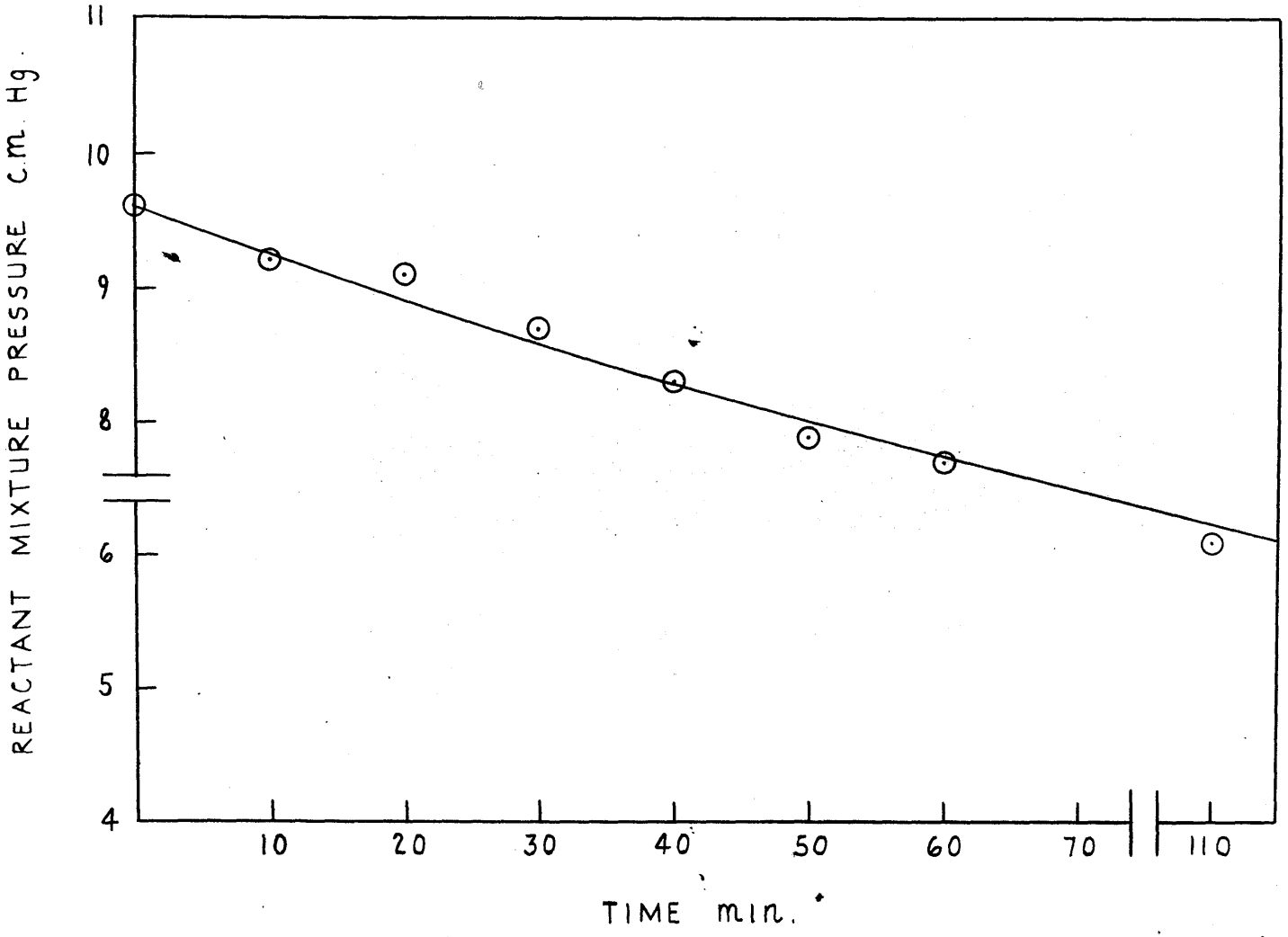


FIG. 22.


REACTANT MIXTURE PRESSURE c.m. Hg.
11
10
9
8
6
5
4
10
20
30
40
50
60
70
110
TIME min.

T A B L E 5

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

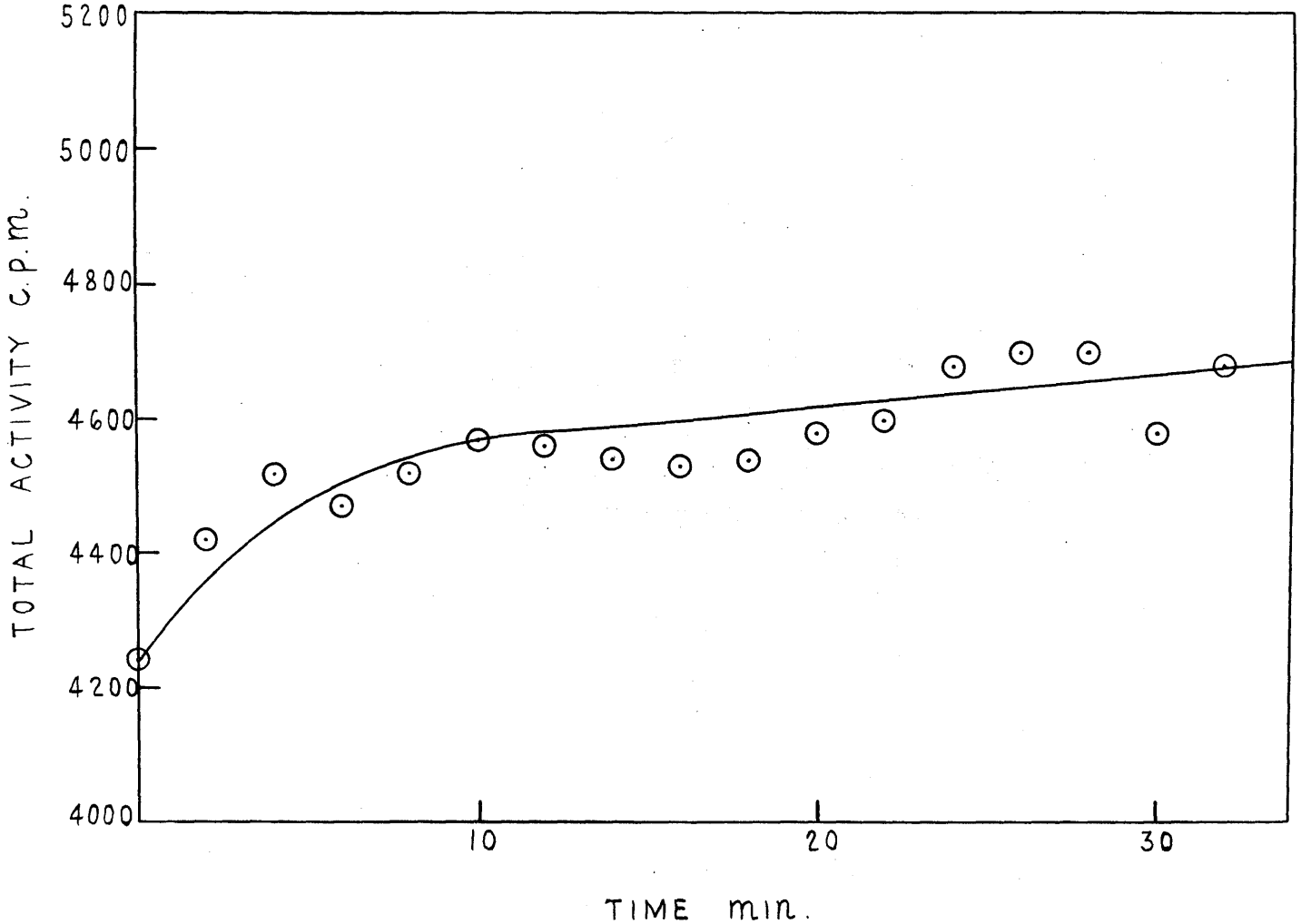
67 mg 5% PALLADIUM ON ALUMINA

ETHYLENE PRESSURE 2.6 cm

TIME * min.	TOTAL ACTIVITY C. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	4242	22	4604
2	4522	24	4679
4	4418	26	4709
6	4468	28	4701
8	4517	30	4576
10	4564	32	4683
12	4561	34	4461
14	4539	36	4660
16	4529	38	4657
18	4542	40	4620
20	4583		

* Time from admission of ethylene

FIG. 23.


5200
5000
4800
4600
4400
4200
4000
TOTAL ACTIVITY c.p.m.
10
20
30
TIME min.

T A B L E 6

FINAL OBSERVED ACTIVITIES OBTAINED FOR PALLADIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	5986	2228	3758	70
B	4626	660	3966	72
C	3645	180	3464	63
D	3638	180	3478	63

* Saturation Activity Corrected For Dead Time 5721 c.p.m.

4. 7. Results for Rhodium Catalyst.

TABLE 7

ADSORPTION ISOTHERM

386 mg 5% RHODIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
2102	1363	739
2470	1751	719

It was thought desirable to determine the effect of bringing the catalyst closer and closer without actually putting it under the G.M. tube window to test the extent to which the gas phase activity observed was independent of contribution from the surface activity.

TABLE 8

GAS PHASE ACTIVITY FOR VARIOUS POSITIONS OF THE CATALYST HOLDER

1428, 1331, 1349

These values are in order of increasing proximity to the catalyst itself which at this point showed a surface activity of 2102 c.p.m. The gas phase counts observed were therefore judged to be true gas phase counts.

TABLE 9

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

386 mg 5% RHODIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg
0	1173	44.3 - 36.0 = 8.3
2	1446	
4	1510	
6	1527	
8	1615	
10	1836	44.0 - 36.3 = 7.7
12	1825	
14	1871	
16	1929	
18	1963	
20	1911	43.8 - 36.5 = 7.3
22	2039	
24	2024	
26	2073	
28	2057	
30	2040	43.6 - 36.7 = 6.9

T A B L E 9 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg
32	2097	
34	2106	
36	2142	
38	2064	
40	2039	43.4 - 36.9 = 6.5
42	2131	
52	2002	43.4 - 37.0 = 6.3
60	2117	
62	2042	
64	2011	43.1 - 37.2 = 5.9
66	2021	
68	2069	
70	2067	
72	2121	
74	2050	43.0 - 37.3 = 5.7
162	2088	42.5 - 37.7 = 4.8

FIG. 24.

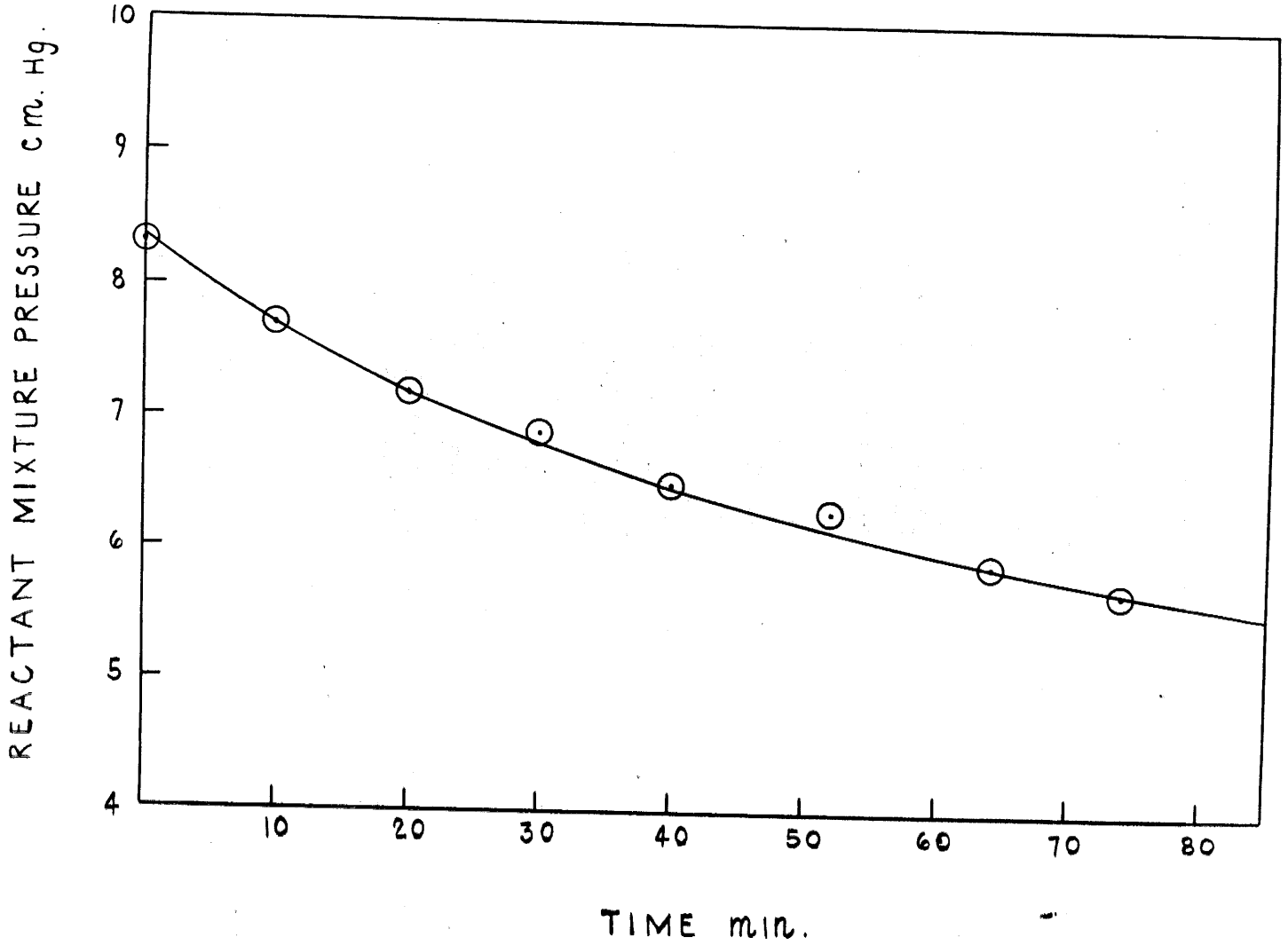
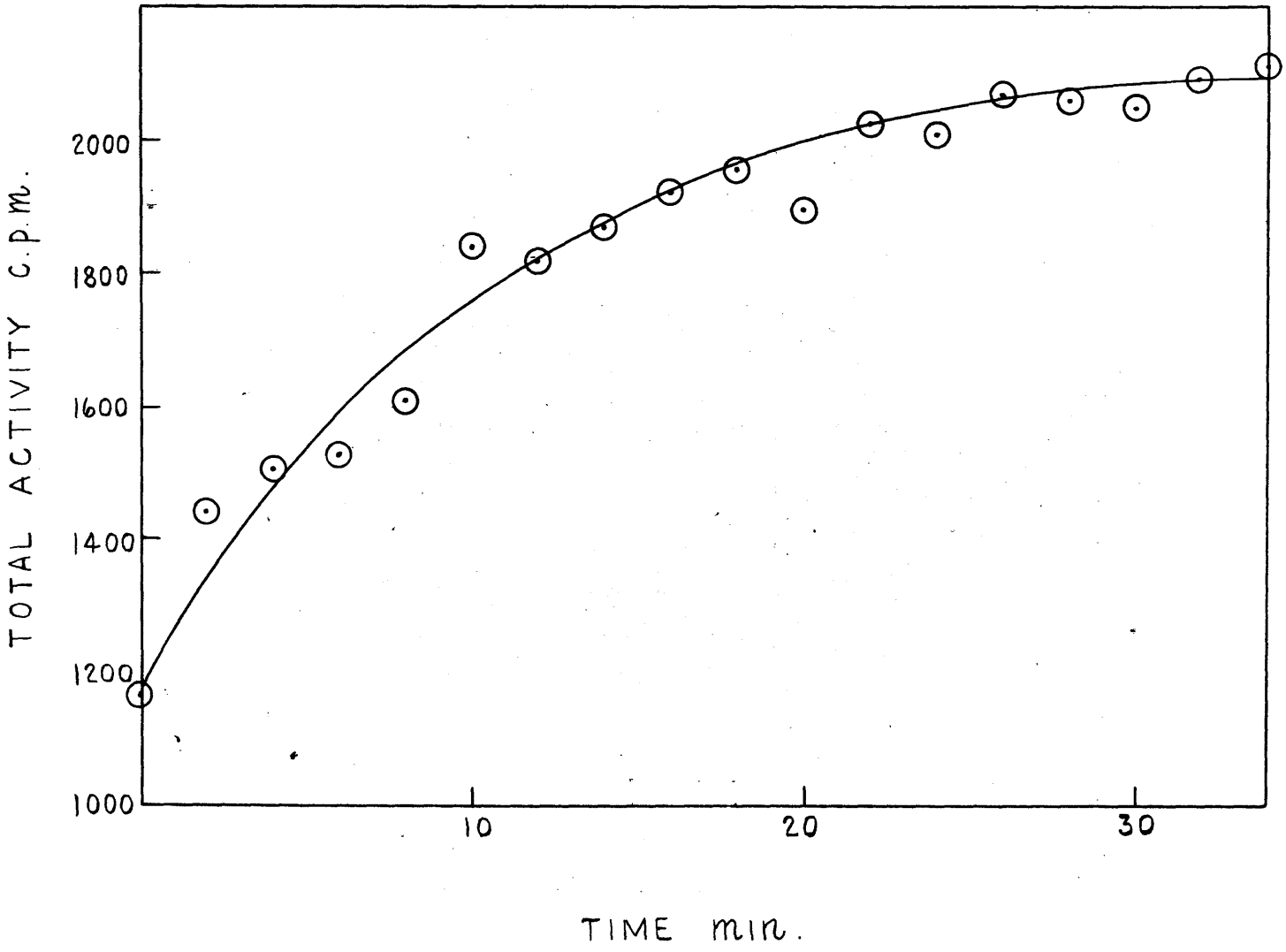

REACTANT MIXTURE PRESSURE cm. Hg.
10
9
8
7
6
5
4
10
20
30
40
50
60
70
80
TIME min.

FIG. 25.


TOTAL ACTIVITY C.P.M.
2000
1800
1600
1400
1200
1000
10
20
30
TIME min.

T A B L E 10

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

386 mg 5% RHODIUM ON ALUMINA

ETHYLENE PRESSURE 4.3 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	1285	26	1638
2	1435	28	1589
4	1536	30	1625
6	1603	32	1641
8	1668	34	1580
10	1693	36	1644
12	1686	38	1707
14	1595	40	1543
16	1710	42	1617
18	1708	52	1621
20	1597	54	1597
22	1674	56	1556
24	1604	58	1588

* Time from Admission of Ethylene.

Since the observed activity rapidly reached a constant value in this case, no total activity-time curve was drawn.

T A B L E 11

FINAL OBSERVED ACTIVITIES OBTAINED FOR RHODIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION ⁎
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	2082	1915	167	23
B	1609	1433	176	24
C	319	189	130	18
D	326	170	156	20

⁎ Saturation Activity Corrected for Dead-Time 753 c.p.m.

4. 8. Results For Platinum Catalyst.

T A B L E 12

ADSORPTION ISOTHERM

283 mg 5% PLATINUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c.p.m.	c.p.m.	c.p.m.
1169	202	967
1680	219	1461
2615	268	2347
4682	343	4339
5830	403	5427
7868	850	7018
8026	1185	6841
8142	1137	7005

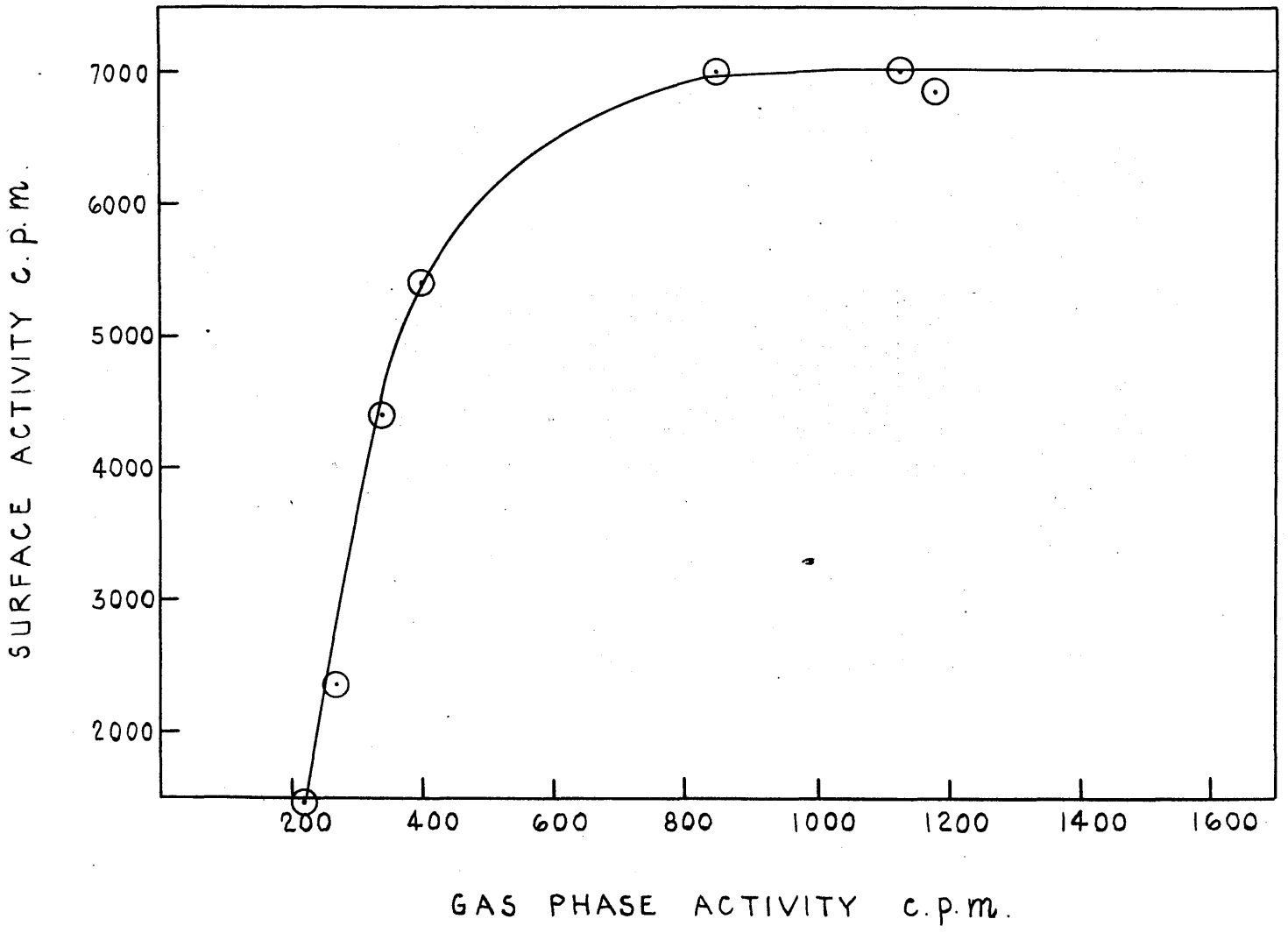
TABLE 13

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

283 mg 5% PLATINUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg
0	6597	44.6 - 34.2 = 10.4
2	5112	
4	4373	
6	4119	
8	3937	
10	3736	44.5 - 34.3 = 10.2
12	3594	
14	3534	
16	3522	
18	3452	
20	3531	44.4 - 34.3 = 10.0
22	3546	
24	3495	

FIG. 27.


SURFACE ACTIVITY c.p.m.
7000
6000
5000
4000
3000
2000
200
400
600
800
1000
1200
1400
1600
GAS PHASE ACTIVITY c.p.m.

T A B L E 13 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg.
26	3554	
28	3571	
30	3506	
32	3488	
34	3500	
36	3422	
38	3508	
40	3421	
42	3556	
44	3526	44.3 - 34.5 = 9.8

FIG. 28.

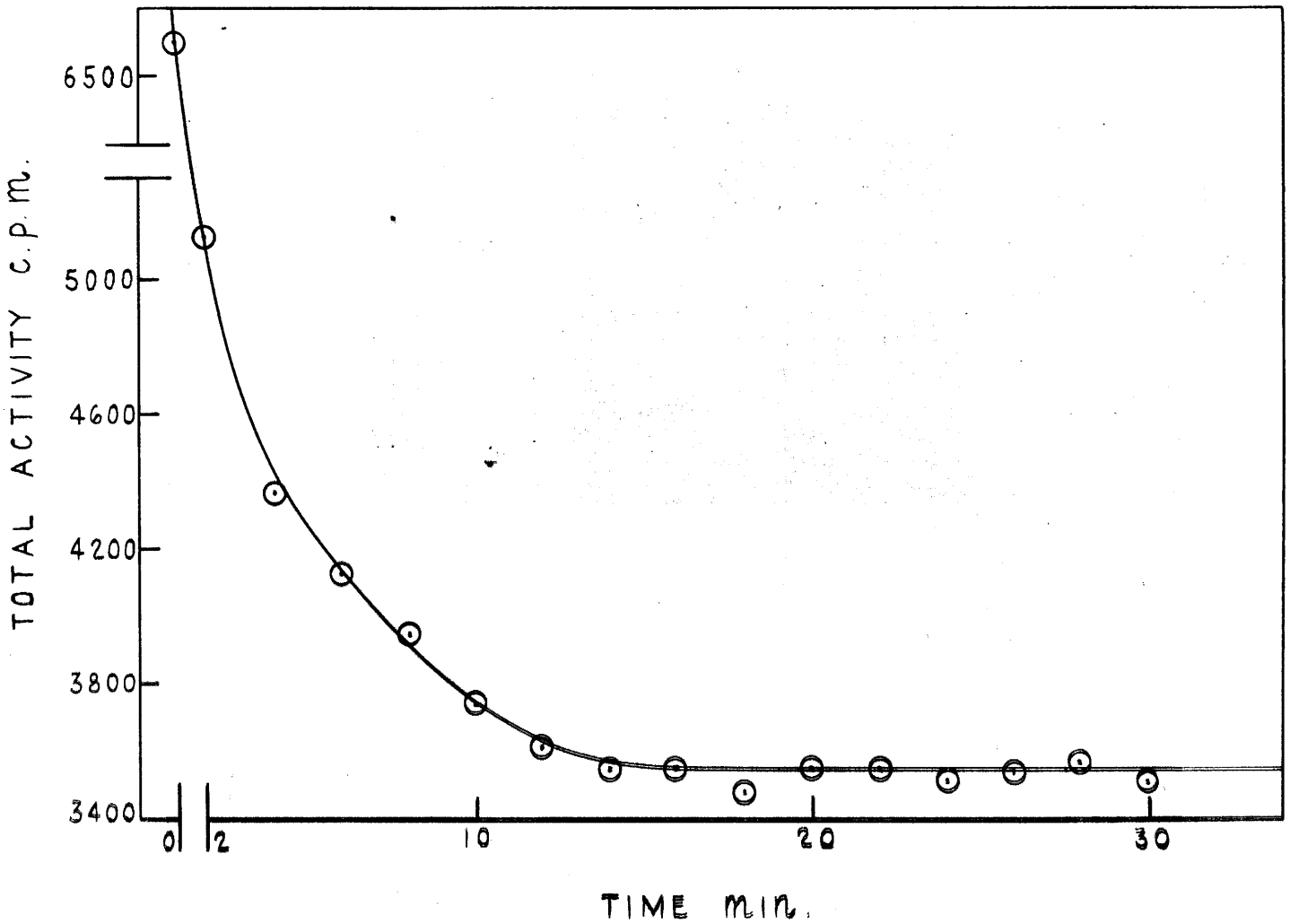
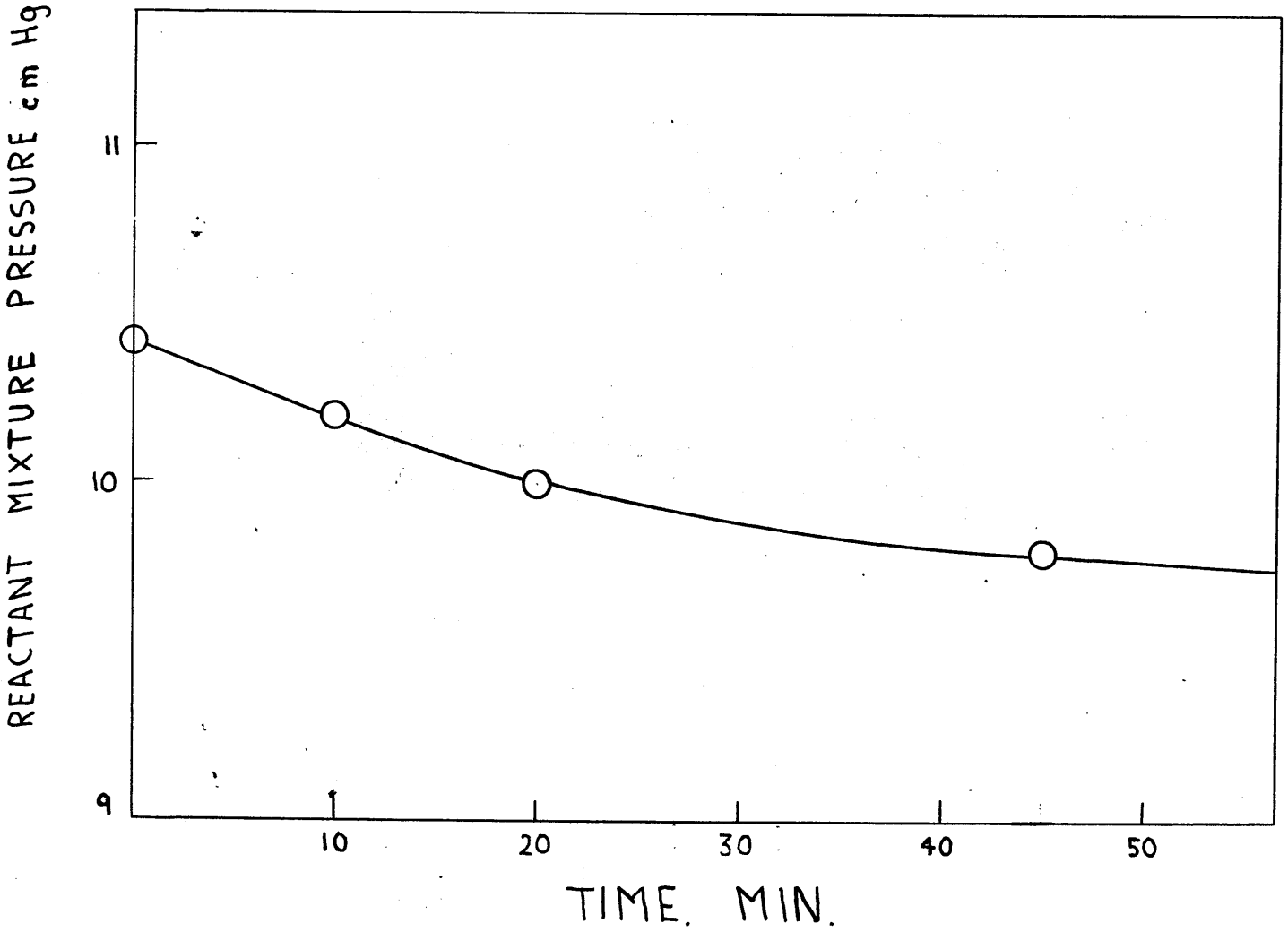

TOTAL ACTIVITY C.P.M.
6500
5000
4600
4200
3800
3400
0
2
10
20
30
TIME min.

FIG. 29.



T A B L E 14

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

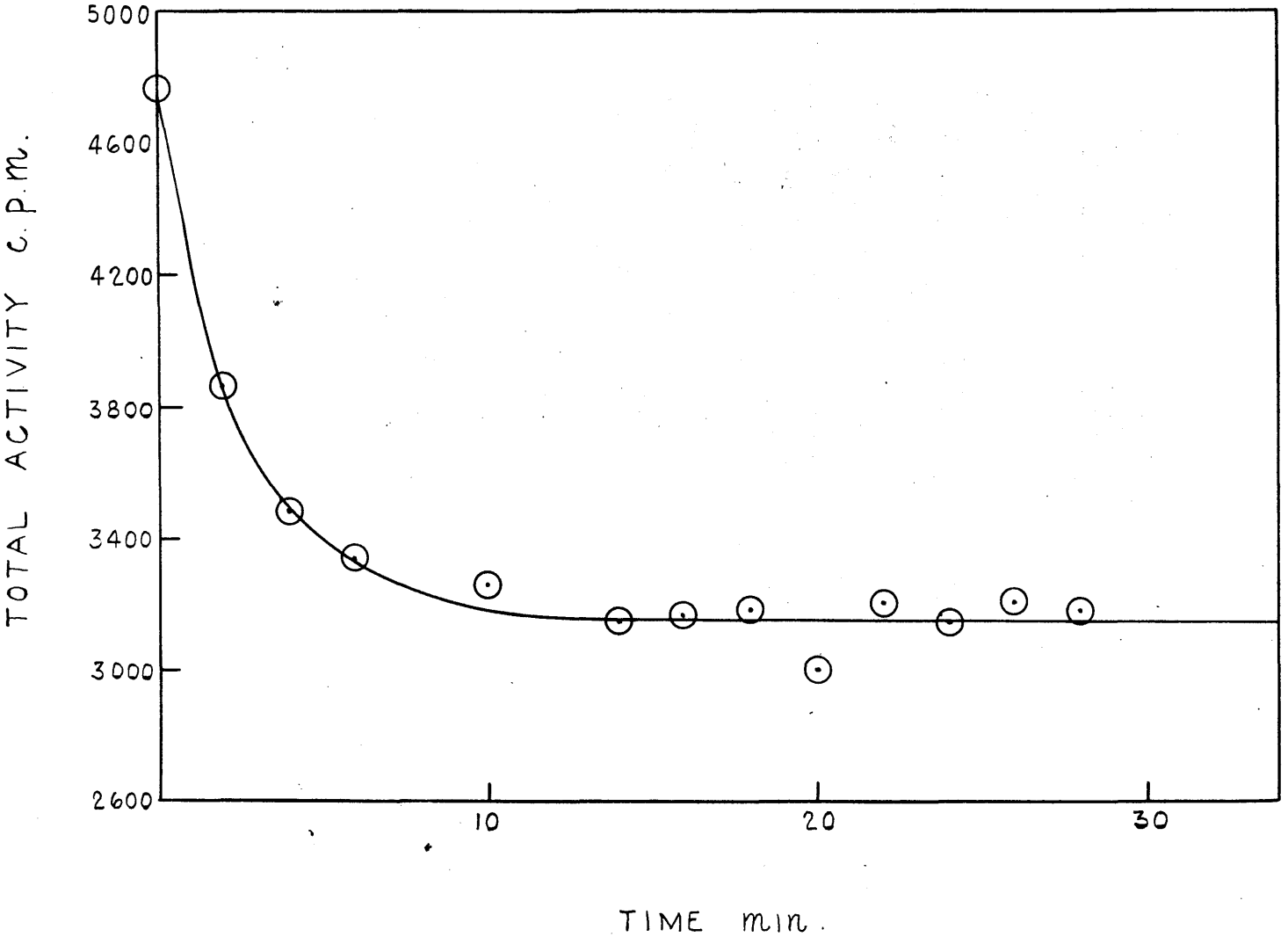
283 mg 5% PLATINUM ON ALUMINA

ETHYLENE PRESSURE 4. 8 cm

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	4764	18	3050
2	3857	20	3222
4	3469	22	3145
6	3328	24	3211
8	3264	52	3185
10	3217	54	3131
12	3120	56	3137
14	3144	58	3074
16	3170	60	3135

* Time From Admission Of Ethylene.

FIG. 30.


TOTAL ACTIVITY c.p.m.
5000
4600
4200
3800
3400
3000
2600
10
20
30
TIME min.

T A B L E 15

FINAL OBSERVED ACTIVITIES OBTAINED FOR PLATINUM

A	ETHYLENE HYDROGENATION
B	ETHYLENE EXCHANGE
C	ADMISSION OF HYDROGEN ALONE
D	EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	3503	3097	406	6
B	3119	2340	779	11
C	2939	2355	584	8
D	.387	170	217	3

* Saturation Activity Corrected for Dead-Time 7490 c.p.m.

4. 9. Results for Iridium Catalyst

T A B L E 16

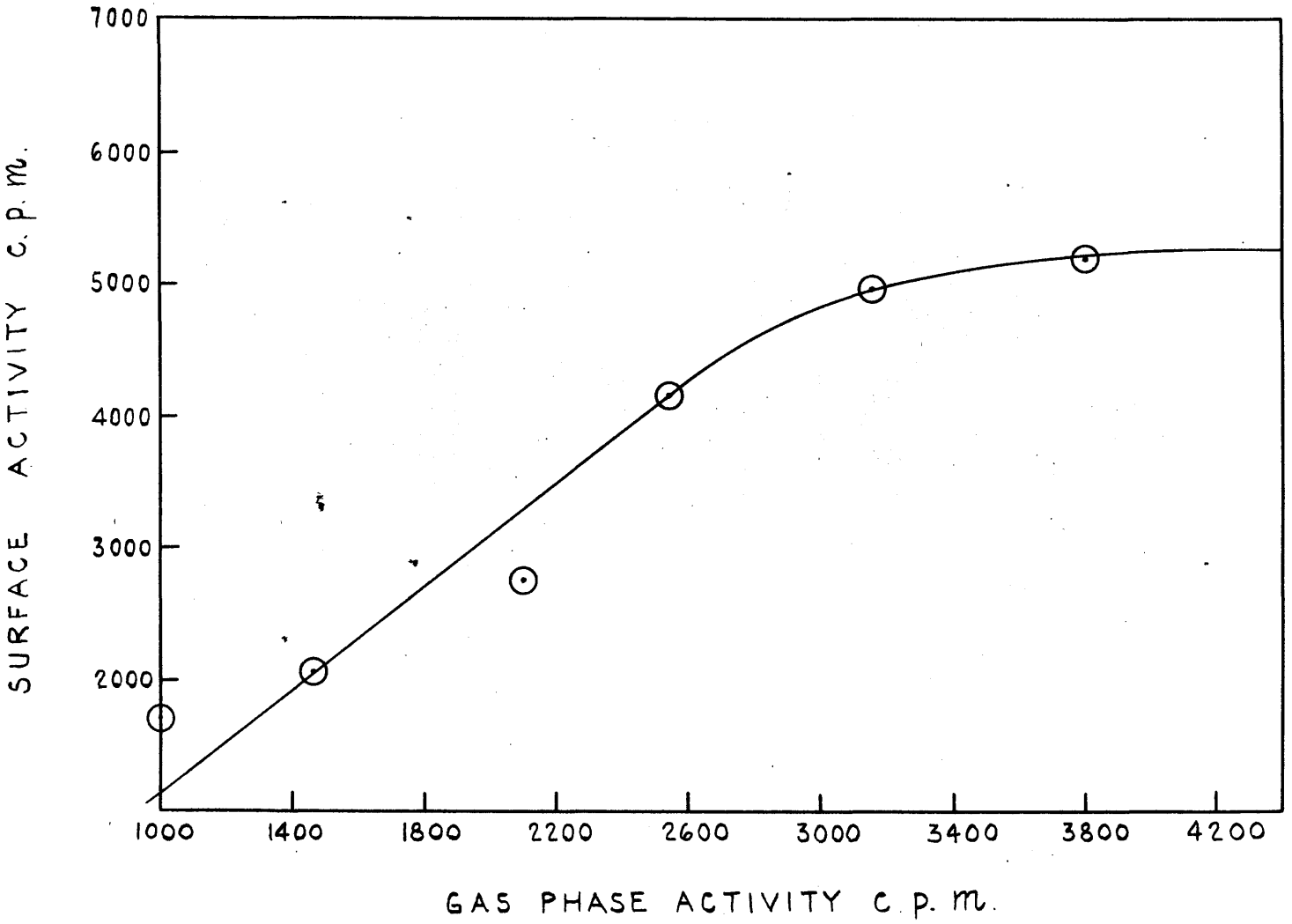
ADSORPTION ISOTHERM

283 mg 5% IRIDIUM ON ALUMINA CATALYST

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1605	552	1053
2591	954	1637
3477	1460	2017
4842	2096	2746
6686	2542	4144
8133	3148	4985
9091	3888	5203

FIG. 31.


7000
6000
5000
4000
3000
2000
SURFACE ACTIVITY C.P.M.
1000
1400
1800
2200
2600
3000
3400
3800
4200
GAS PHASE ACTIVITY C.P.M.

T A B L E 17

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

283 mg 5% IRIDIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg.
0	7629	43.1 - 35.7 = 7.4
2	8308	
4	8009	
6	8216	
8	8420	
10	8559	
12	8498	
14	8766	
16	8772	
18	8938	
20	8853	
22	9137	

T A B L E 17 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm Hg
24	9199	
26	9161	
28	9103	
30	9104	
32	9151	
40	9281	43.0 - 35.8 = 7.2
120	9209	
122	8903	
124	8950	
126	9087	
128	9176	

FIG. 32.

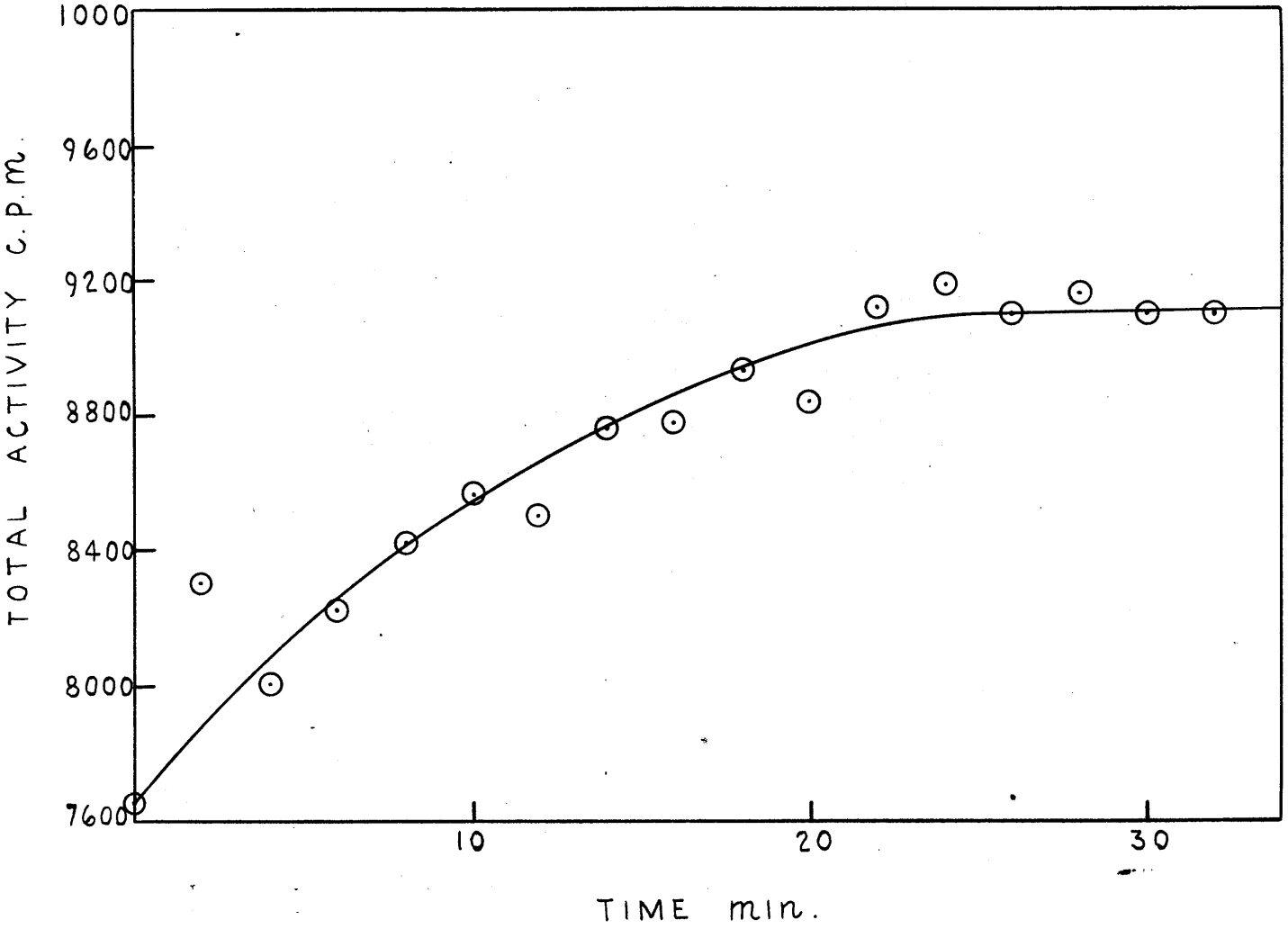
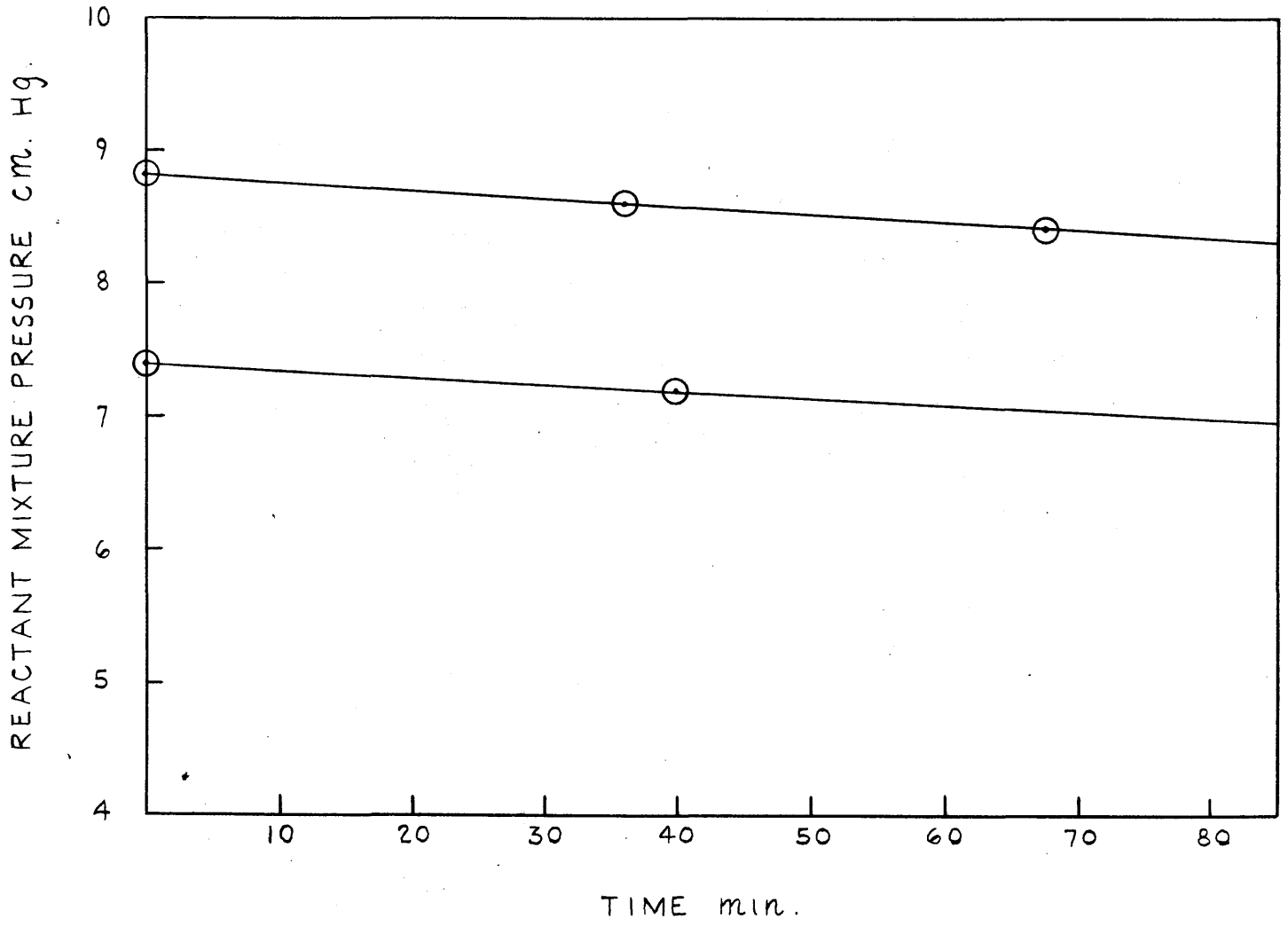

1000
9600
9200
8800
8400
8000
7600
TOTAL ACTIVITY C.P.M.
10
20
30
TIME min.

FIG. 33.


REACTANT MIXTURE PRESSURE cm. Hg.
10
9
8
7
6
5
4
10
20
30
40
50
60
70
80
TIME min.

T A B L E 18

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

283 mg 5% IRIDIUM ON ALUMINA CATALYST

ETHYLENE PRESSURE 3.3 cm Hg

TIME * min.	TOTAL COUNT RATE c. p. m.	TIME min.	TOTAL COUNT RATE c. p. m.
0	5294	12	5188
2	5208	14	5213
4	5212	16	5290
6	5185	18	5198
8	5204	20	5269
10	5202		

* Time from Admission of Ethylene

Since the observed total activity was seen to be constant with respect to time, no total activity-time curve was drawn in this case.

TABLE 19

FINAL OBSERVED ACTIVITIES OBTAINED FOR IRIDIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	9078	4442	4636	92
B	5242	992	4250	80
C	4059	180	3879	71
D	4072	180	3792	71

* Saturation Activity Corrected for Dead-Time 5654 c.p.m.

4. 10 Results for Nickel Catalyst

T A B L E 20

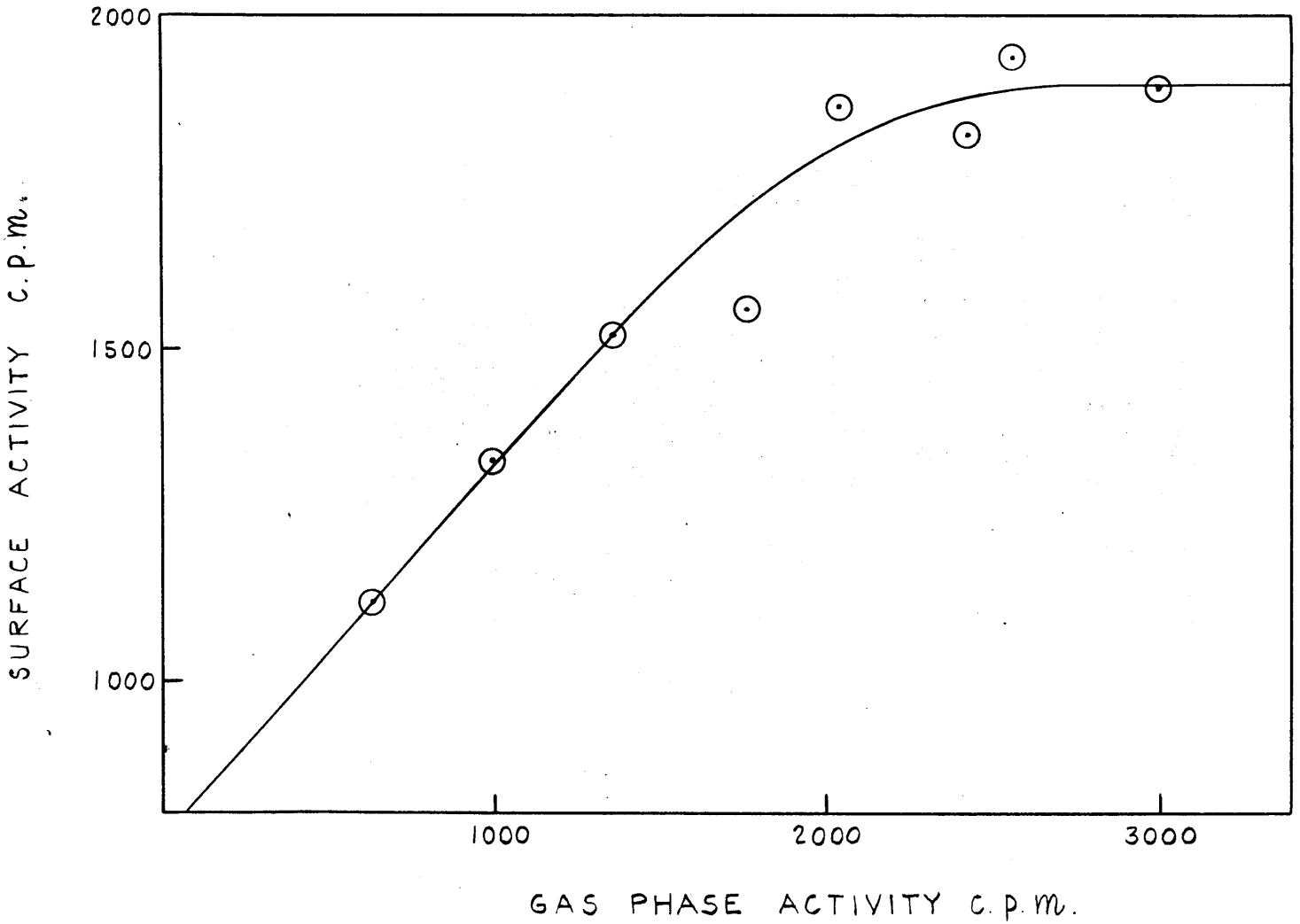
ADSORPTION ISOTHERM

407 mg 5% NICKEL ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1243	408	835
1736	615	1121
2422	994	1328
2992	1375	1517
3346	1786	1560
3913	2047	1865
4241	2425	1816
4512	2576	1936
4916	3018	1898

FIG. 34.


2000
1500
1000
SURFACE ACTIVITY C.P.M.
1000
2000
3000
GAS PHASE ACTIVITY C.P.M.

T A B L E 21

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

407 mg 5% NICKEL ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT GASES
min.	c. p. m.	cm. Hg
0	2446	44.2 - 36.8 = 7.4
2	2952	
4	3069	
6	3253	
8	3480	
10	3636	44.1 - 36.9 = 7.2
12	3791	
14	3958	
16	4019	
18	3994	
20	4255	44.0 - 37.0 = 7.0

T A B L E 21 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT GASES
min.	c. p. m.	cm Hg
22	4351	
24	4285	
26	4375	
28	4410	
30	4530	43.9 - 37.1 = 6.8
32	4623	
60	4641	

FIG. 35.

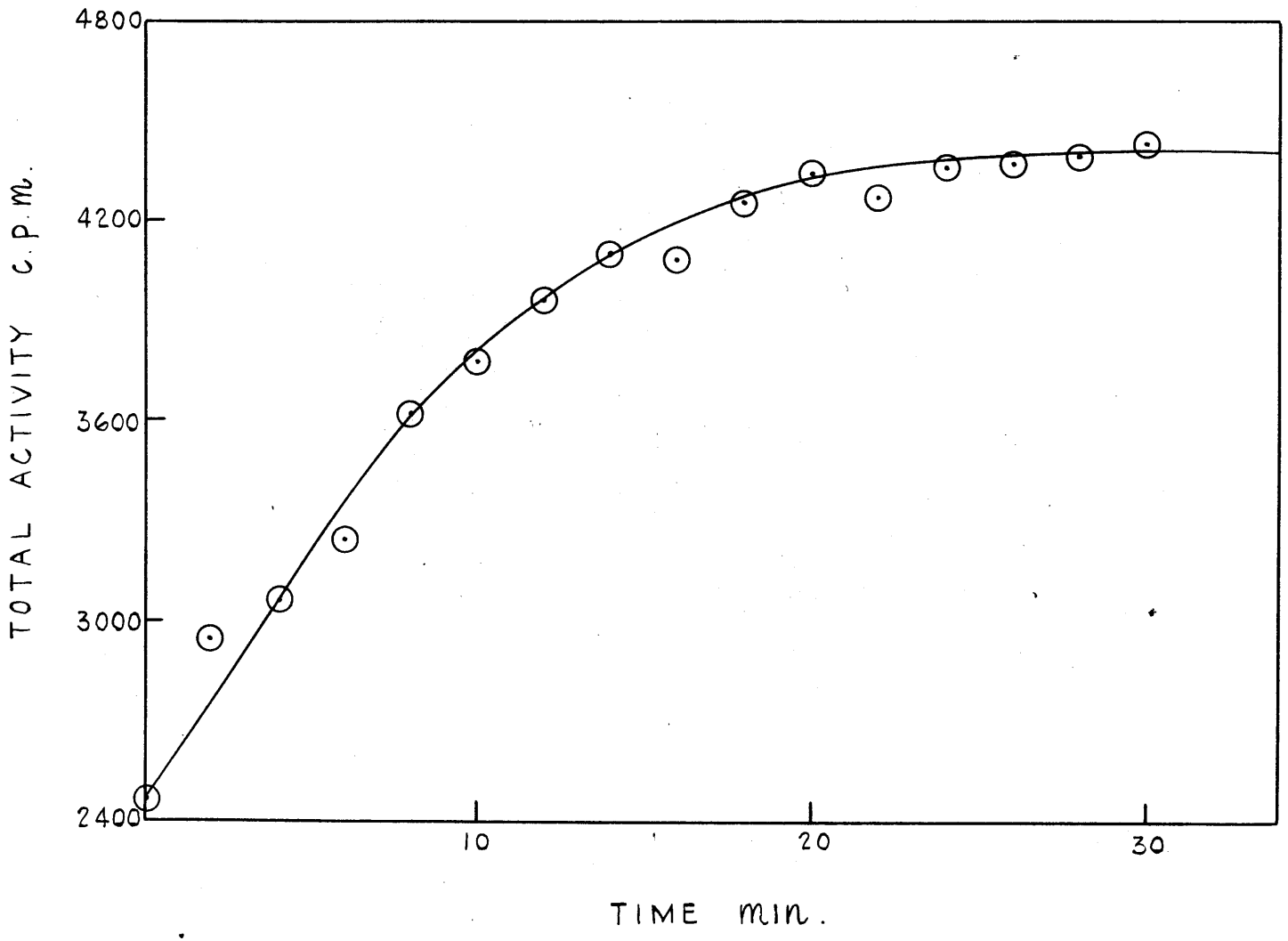
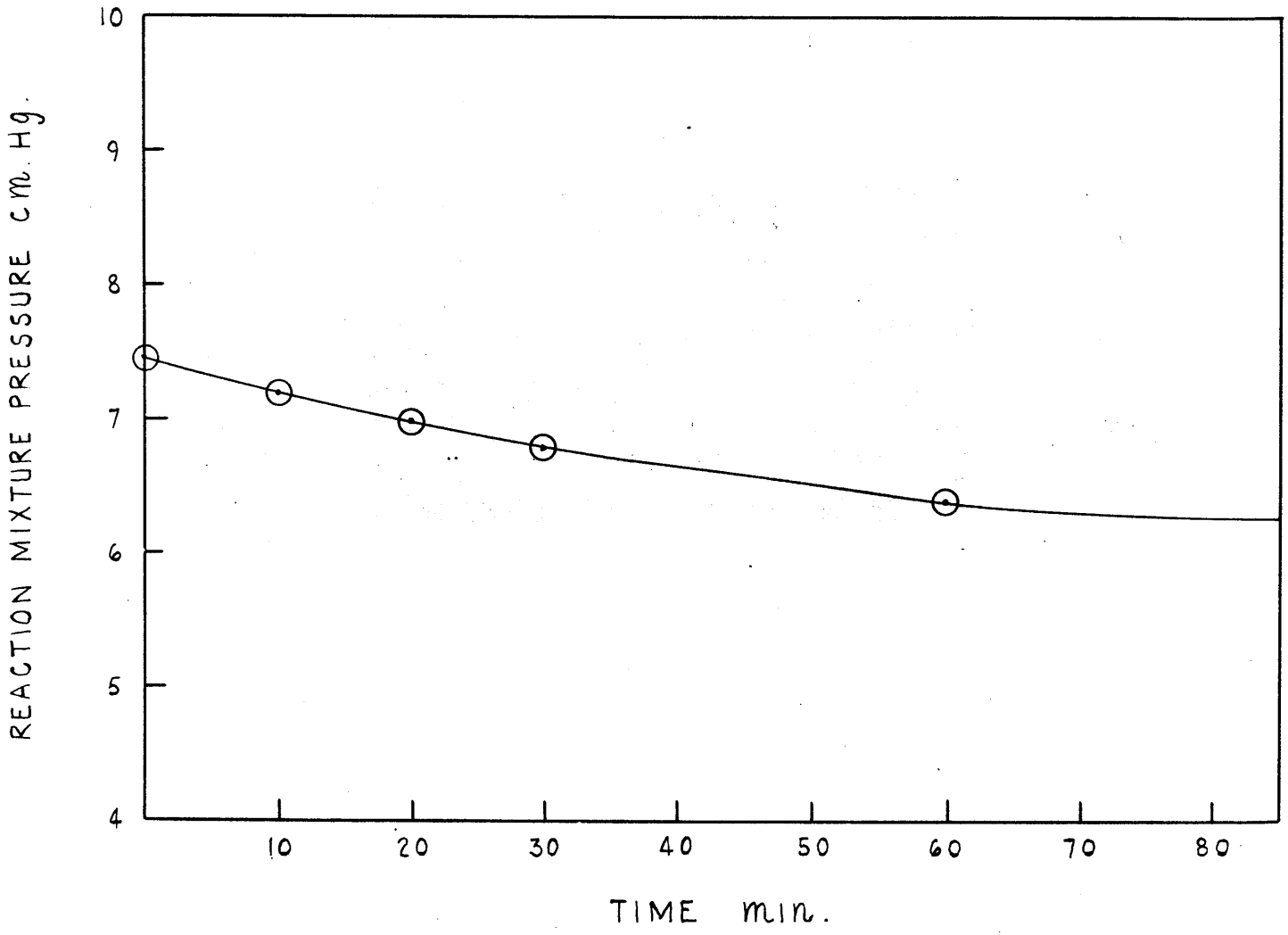


FIG. 36.


REACTION MIXTURE PRESSURE CM. Hg.
10
9
8
7
6
5
4
10
20
30
40
50
60
70
80
TIME min.

T A B L E 22

CHANGE IN OBSERVED TOTAL ACTIVITY RATE WITH TIME FOR EXCHANGE

407 mg 5% NICKEL ON ALUMINA

ETHYLENE PRESSURE 3.3 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	2003	18	3618
2	2418	20	3541
4	2754	22	3545
6	2913	24	3661
8	3072	26	3647
10	3284	28	3735
12	3341	30	3642
14	3489	32	3543
16	3507	34	3643

* Time from Admission of Ethylene

FIG. 37.

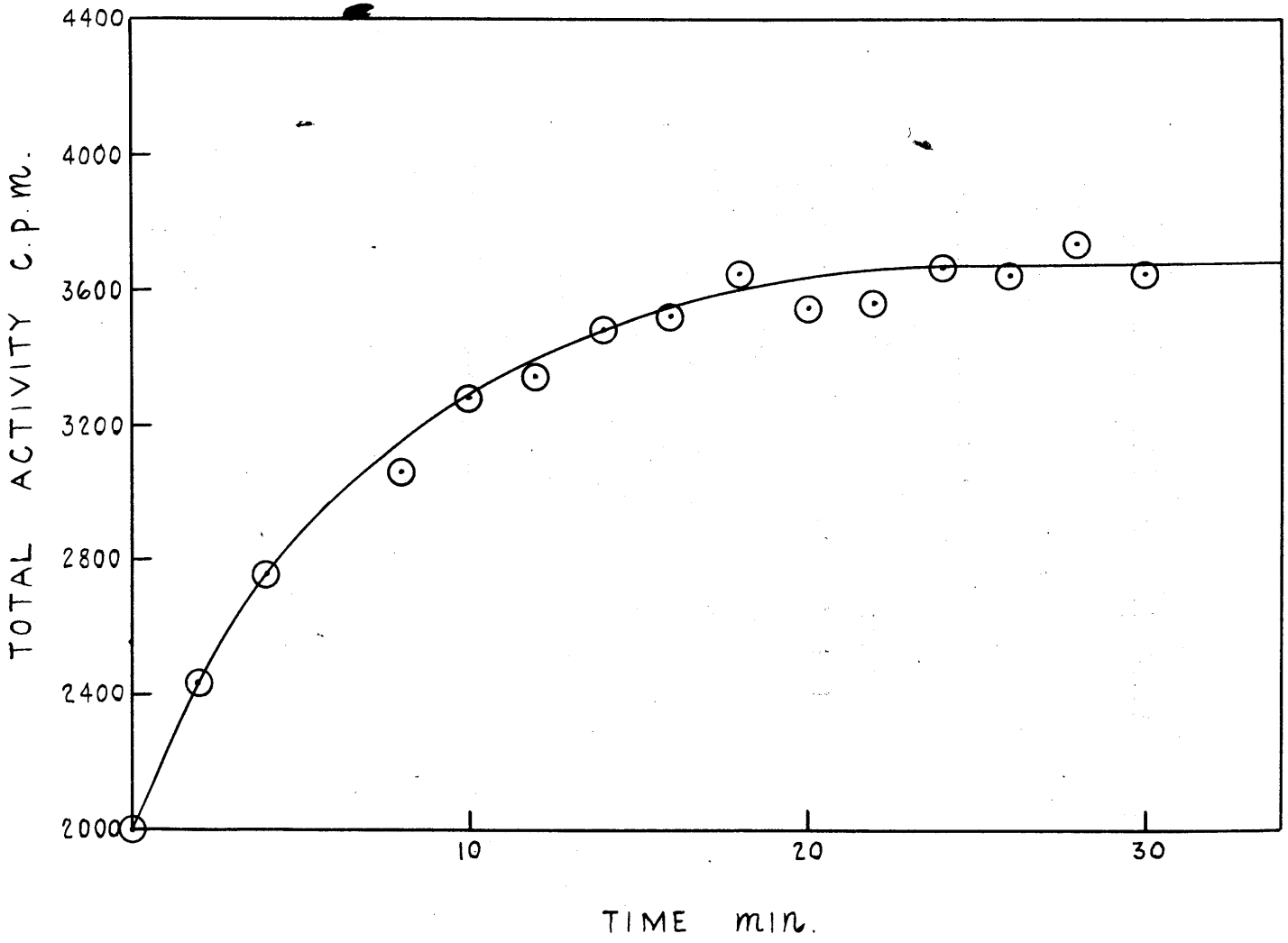

4400
4000
3600
3200
2800
2400
2000
TOTAL ACTIVITY C.P.M.
10
20
30
TIME min.

TABLE 23

FINAL OBSERVED ACTIVITIES OBTAINED FOR NICKEL

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
A	4748	4249	499	26
B	3609	3100	509	26
C	727	234	493	24
D	783	273	510	25

* Saturation Activity Corrected for Dead-Time 2041 c.p.m.

4. 11. Adsorption on Alumina

Since the support material in the catalysts studied was alumina it was felt necessary to determine whether or not alumina itself adsorbed ethylene.

Up to this point our technique has been employed to compare retention precentages for single catalyst preparations. It has not been necessary to compare extents of initial adsorption. This is essentially what is required now. It is necessary to know if the alumina support is responsible for a significant proportion of the adsorption observed in the catalyst preparations.

At first sight it may be expected that surface activities for the same adsorbing material will be proportional to the weight of this material taken, so that equal weights will give equal adsorption activities. If this were so it would be necessary only to observe adsorption on the same weight of alumina as is present in a catalyst to see if the adsorption on alumina were comparatively significant.

However this proportional relationship fails because of the impossibility of spreading the two samples in question in exactly the same way over the catalyst holder. In other words the counting geometry is not constant.

With these reservations in mind an experiment was carried out along the usual lines. 154 mg of alumina mixed with $\frac{1}{3}$ its

weight of the montmorillonite preparation was reduced for six hours at 500° C and outgassed for a further six hours. This was followed by overnight pumping.

The adsorption isotherm data subsequently obtained is shown in table 24 and graphed in fig. 38. An exchange reaction with non-radioactive ethylene was then carried out, table 25, fig. 39. The final activities obtained are shown in table 26.

At this point it was decided to add to the measuring devices, the McLeod gauge described earlier. This gave a measure of the gas pressure at saturation. The value in the case of alumina is given in table 26.

4. 12 Results for Alumina

T A B L E 24

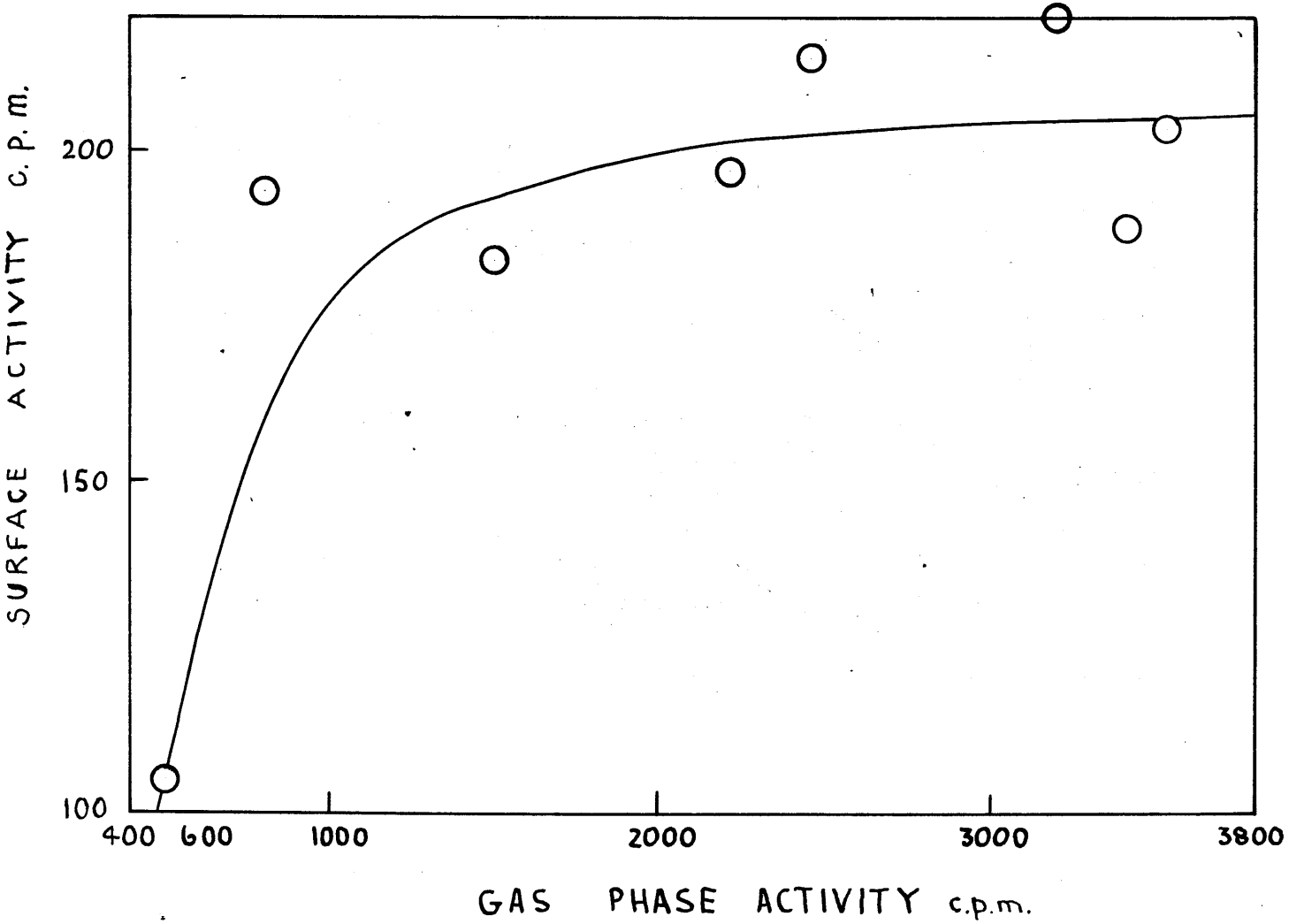
ADSORPTION ISOTHERM

154 mg ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
615	510	105
1000	806	194
1694	1511	183
2413	2216	197
2651	2437	214
3439	3218	221
3605	3417	188
3744	3541	203

FIG. 38.


SURFACE ACTIVITY c.p.m.
200
150
100
400
600
1000
2000
3000
3800
GAS PHASE ACTIVITY c.p.m.

T A B L E 25

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

154 mg ALUMINA

ETHYLENE PRESSURE 6.1 cm

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min,	c. p. m.
0	1323	26	3476
2	1750	28	3484
4	2012	30	3442
6	2147	32	3455
8	2284	34	3651
10	2416	36	3739
12	2682	38	3711
14	2817	40	3600
16	2926	42	3659
18	3207	44	3667
20	3099	46	3707
22	3189	48	3667
24	3418	50	3691

* Time from Admission of Ethylene

FIG. 39.

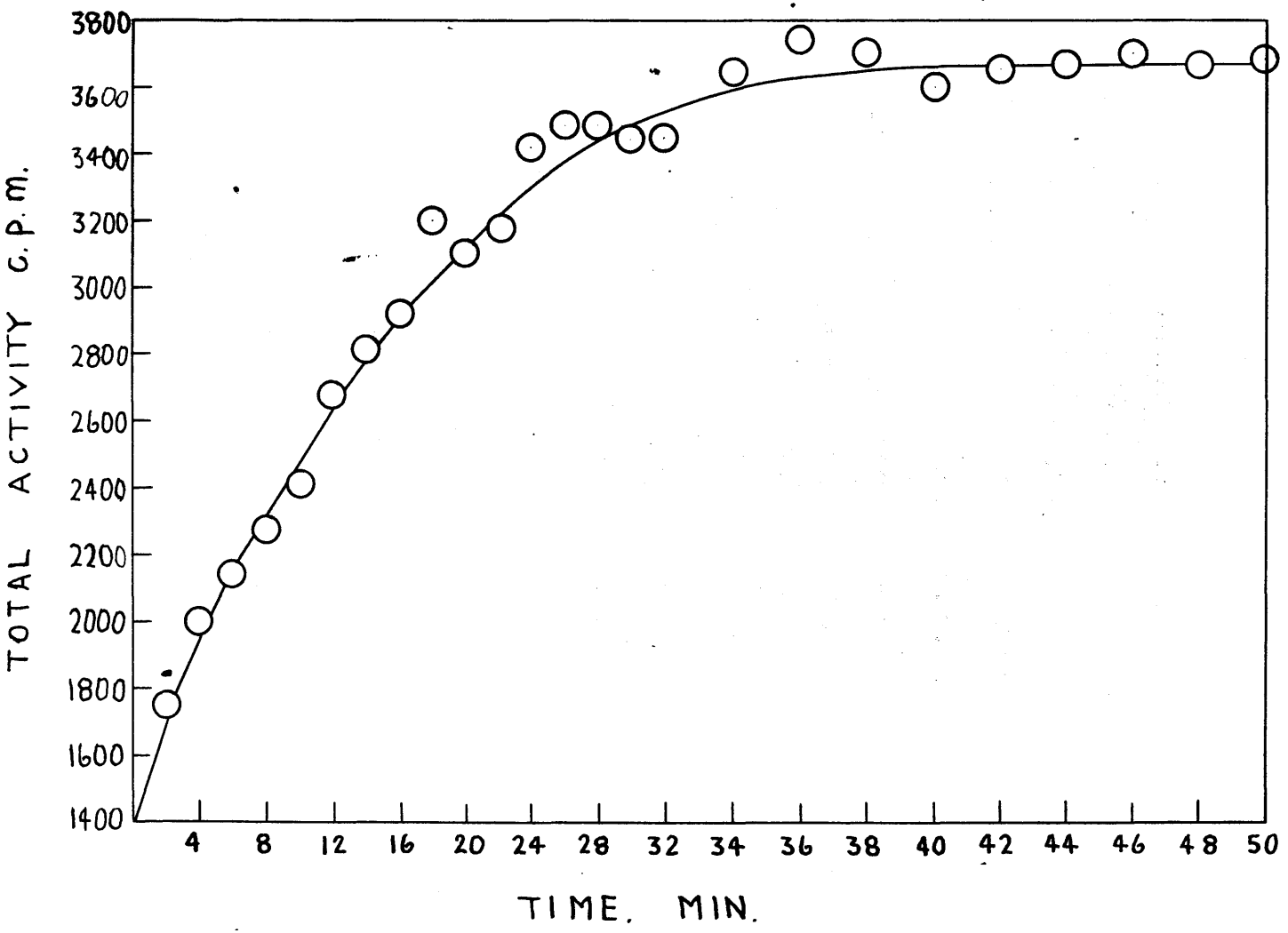

TOTAL ACTIVITY C.P.M.
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
4
8
12
16
20
24
28
32
34
36
38
40
42
44
46
48
50
TIME. MIN.

TABLE 26

FINAL OBSERVED ACTIVITIES OBTAINED WITH ALUMINA

ETHYLENE EXCHANGE

TOTAL	GAS PHASE	SURFACE	RETENTION *
c. p. m.	c. p. m.	c. p. m.	%
3665	3657	8	7

* Saturation Activity Corrected for Dead-Time 215 c. p. m.

Saturation Pressure 4.7×10^{-2} mm.

4. 13. Conclusion to the alumina experiments

Although, as pointed out in section 4.11 it is not possible to arrive at an absolute answer to the question in mind some indication may be obtained from comparing the absolute values of total, gas phase and surface activities together with the ratio of gas phase to surface activity in the case of alumina with the corresponding values for the catalysts already studied.

This information is set out in table 27.

T A B L E 27

ADSORBENT	OBSERVED ACTIVITIES			APPROX. RATIO	REF.
	TOTAL	GAS PHASE	SURFACE	GAS PHASE/SURFACE	
alumina	3744	3541	203	17.	4.12
Pd-catalyst	7372	2069	5303	0.39	4.6
Rh-catalyst	2470	1751	719	2.4	4.7
Pt-catalyst	8142	1137	7005	0.16	4.8
I_r-catalyst	9091	3888	5203	0.75	4.9
Ni-catalyst	4916	3018	1898	1.6	4.10

From this summary it can be seen that not only is the surface activity less for alumina than for any other surface but the ratio of gas phase to surface activity is greater. Also as compared with rhodium and nickel which have the next largest ratios, the gas phase activity is greater.

With the reservations made in section 4. 11 then, it may be concluded that adsorption on alumina itself is low compared with that on the catalysts studied.

There is of course the further reservation that in the presence of the metals the adsorption on alumina may be increased. This point applied also to the extent of retention after exchange, table 26, where it is stated that this is 7%. This figure was arrived at on the basis of a difference of 8 c. p. m. in a total activity of 3665 c. p. m. and thus is probably not significant.

We may conclude therefore that adsorption of ethylene and its retention on alumina itself are both low and consequently that the results obtained for the catalysts do not have to be modified to account for these factors.

4. 14 Introduction to confirmatory experiments.

At this point it was decided to repeat all the catalyst experiments previously described. The results here are presented as before except that no graphs have been drawn. Initially in each sub-section there is the adsorption isotherm data showing saturation of the surface as before. This is followed by the total activity time curves showing finally constant total activity. The shapes of these curves vary again and are assumed to be due to the same effects as those discussed in section 4. 4.

As a result of the lack of constant counting geometry, referred to in section 4. 11, from one experiment to another it is not to be expected that surface activities in these repeat experiments will be comparable in value with those obtained previously. For the same reason it is not possible to fit the gas phase and surface activities to specific adsorption isotherms.

This variable counting geometry may also result in total activity-time curves being of different shapes in the case of one catalyst.

However the percentage retention of pre-adsorbed material can be accurately computed from relative observations and this is done in the following sections as before.

McLeod gauge readings of gas pressure over the saturated catalysts are included in the results which follow.

4. 15. Results for nickel catalyst.

T A B L E 28

ADSORPTION ISOTHERM

343 mg 5% NICKEL ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1684	283	1401
1946	378	1568
2877	842	2035
3747	1250	2497
4059	1512	2547
4330	1693	2637

TABLE 29

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

343 mg 5% NICKEL ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	4071	45.8 - 35.2 = 10.6
2	3882	
4	3542	
6	3282	
8	3352	
10	3189	45.7 - 35.2 = 10.4
12	3092	
14	3172	
16	3222	
18	3040	
20	3101	45.6 - 35.4 = 10.2
22	2979	
24	3181	
26	3017	
28	3032	
30	3090	45.5 - 35.5 = 10.0
32	2990	

T A B L E 30

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

343 mg 5% NICKEL ON ALUMINA

ETHYLENE PRESSURE 4.8 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	1542	18	1453
2	1593	20	1514
4	1558	22	1500
6	1438	24	1457
8	1491	26	1473
10	1454	28	1371
12	1394	30	1417
14	1434	32	1435
16	1465		

* Time from Admission of Ethylene.

TABLE 31

FINAL OBSERVED ACTIVITIES OBTAINED FOR NICKEL

A	ETHYLENE HYDROGENATION
B	ETHYLENE EXCHANGE
C	ADMISSION OF HYDROGEN ALONE
D	EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	3037	2469	568	22
B	1437	838	599	22
C	545	58	487	18
D	524	56	468	17

* Saturation Activity Corrected for Dead Time 2719 c. p. m.

Saturation Pressure 1.1 X 10^{-1} mm.

4. 16 Results for platinum catalyst

T A B L E 32

ADSORPTION ISOTHERM

249 mg 5% PLATINUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
392	100	292
771	157	614
964	214	750
1167	316	851
1322	340	982
1406	439	1027

T A B L E 33

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

249 mg 5% PLATINUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	963	45.9 - 35.3 = 10.6
2	875	
4	787	
6	750	
8	733	
10	717	45.8 - 35.4 = 10.4
12	675	
14	651	
16	654	
18	680	
20	656	45.7 -35.5 = 10.2
22	657	
24	675	
26	664	
28	658	
30	672	45.6 - 35.6 = 10.0
32	661	

T A B L E 34

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

249 mg 5% PLATINUM ON ALUMINA

ETHYLENE PRESSURE 5.1 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	440	18	267
2	350	20	263
4	334	22	257
6	306	24	268
8	296	26	265
10	247	28	262
12	251	30	277
14	283	32	264
16	293		

* Time from Admission of Ethylene

T A B L E 35

FINAL OBSERVED ACTIVITIES OBTAINED FOR PLATINUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c. p. m.	c. p. m.	c. p. m.	%
A	665	298	67	7
B	267	173	94	9
C	108	45	63	6
D	104	45	59	6

* Saturation Activity Corrected for Dead-Time 1020 c. p. m.

Saturation Pressure 4.0×10^{-2} mm.

4. 17 Results for rhodium catalysts.

T A B L E 36

ADSORPTION ISOTHERM

248 mg 5% RHODIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
605	478	127
939	713	226
1374	1077	297
1683	1341	342
2060	1675	385
2283	1979	304
2503	2122	381

T A B L E 37

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

248 mg 5% RHODIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	1303	45.3 - 35.8 = 9.5
2	1453	
4	1592	
6	1572	
8	1600	
10	1713	4419 - 36.2 = 8.7
12	1834	
14	1878	
16	1885	
18	1983	
20	1978	44.5 - 36.6 = 7.9

T A B L E 37 (continued)

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
22	2246	
24	2208	
26	2210	
28	2315	
30	2269	44.2 - 37.0 = 7.2
32	2272	
34	2279	
36	2408	
38	2354	
40	2450	44.0 - 37.2 = 6.8
42	2342	

a Time from Admission of Ethylene

T A B L E 38

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

248 mg 5% RHODIUM ON ALUMINA

ETHYLENE PRESSURE 5.0 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	619	18	807
2	750	20	840
4	707	22	778
6	717	24	864
8	781	26	849
10	792	28	834
12	797	30	809
14	804	35	843
16	807	40	842

* Time from Admission of Ethylene

T A B L E 39

FINAL OBSERVED ACTIVITIES OBTAINED FOR RHODIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c. p. m.	c. p. m.	c. p. m.	%
A	2398	2326	72	21
B	863	766	97	27
C	314	225	89	24
D	308	223	85	24

* Saturation activity corrected for dead-time 365 c. p. m.

Saturation pressure 7.8×10^{-2} mm.

4. 18. Results for Iridium Catalyst.

T A B L E 40

ADSORPTION ISOTHERM

279 mg 5% IRIDIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
830	247	583
1788	422	1366
3827	533	3294
4159	580	3529
4293	712	3581

TABLE 41

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

279 mg 5% IRIDIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	3222	44.8 - 36.3 = 8.5
2	2801	
4	2475	
6	1907	
8	1403	
10	1449	44.7 - 36.4 = 8.3
12	1436	
14	1328	
16	1442	
18	1338	
20	1318	44.6 - 36.5 = 8.1
22	1318	
24	1334	
26	1312	
28	1317	
30	1306	44.5 - 36.3 = 7.9
32	1295	

T A B L E 42

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

279 mg 5% IRIDIUM ON ALUMINA

ETHYLENE PRESSURE

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min,	c. p. m.	min.	c. p. m.
0	998	18	683
2	834	20	695
4	793	22	729
6	753	24	734
8	764	26	714
10	728	28	668
12	756	80	682
14	712	82	721
16	706		

* Time from Admission of Ethylene

T A B L E 43

FINAL OBSERVED ACTIVITIES OBTAINED FOR IRIDIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	1317	831	486	13
B	669	265	434	12
C	386	76	310	8
D	350	76	278	7

* Saturation Activity Corrected For Dead Time 3729 c. p. m.

Saturation Pressure 3.4×10^{-2} mm.

4. 19. Further Results for Iridium Catalysts.

Since the retention figures hereare so different from those of section 4. 9. this experiment was repeated on another sample of the iridium catalyst.

TABLE 44

ADSORPTION ISOTHERM

284 mg 5% IRIDIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1224	26	1198
2604	32	2572
5472	84	5388
6702	114	6588
8450	219	8231
9386	356	9030
10794	583	10211
1,911	1.129	10,782

T A B L E 45

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

284 mg 5% IRIDIUM ON ALUMINA

TIME	TOTAL	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	7842	45.9 - 35.2 = 10.7
2	6552	
4	5918	
6	5612	
8	5276	
10	5082	45.8 - 35.2 = 10.5
12	4929	
14	4882	
16	4615	
18	4656	
20	4692	45.7 - 35.4 = 10.3
22	4666	
24	4564	
26	4458	
28	4465	
30	4557	45.6 - 35.5 = 10.1
32	4496	

T A B L E 46

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

284 mg 5% IRIDIUM ON ALUMINA

ETHYLENE PRESSURE 5.3 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	3230	18	2464
2	2875	20	2451
4	2791	22	2593
6	2607	24	2502
8	2686	26	2439
10	2633	28	2391
12	2583	30	2418
14	2528	32	2410
16	2481		

* Time from Admission of Ethylene

TABLE 47

FINAL OBSERVED ACTIVITIES OBTAINED FOR IRIDIUM

A ETHYLENE HYDROGENATION

B ETHYLENE EXCHANGE

C ADMISSION OF HYDROGEN ALONE

D EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	4492	2054	2438	22
B	2414	495	1919	17
C	1050	147	903	8
D	2009	47	1962	17

* Saturation Activity Corrected for Dead Time 11679 c. p. m.

Saturation Pressure 1.1×10^{-2} mm.

4. 20 Results for Palladium Catalysts.

TABLE 48

ADSORPTION ISOTHERM

109 mg 5% PALLADIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
219	115	104
385	234	151
617	359	258
749	484	265

T A B L E 49

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

109 mg 5% PALLADIUM ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	662	45.1 -36.0 = 9.1
2	622	
4	669	
6	611	
8	631	
10	628	44.9 - 36.2 = 8.7
12	637	
14	623	
16	607	
18	654	
20	604	44.7 - 36.4 = 8.3
22	655	
24	605	
26	640	
28	661	
30	642	44.6 - 36.5 = 8.1
32	677	

T A B L E 50

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

109 mg 5% PALLADIUM ON ALUMINA

ETHYLENE PRESSURE 3.8 cm

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	633	18	627
2	632	20	633
4	599	22	622
6	641	24	634
8	657	26	631
10	655	28	626
12	631	30	635
14	637	32	627
16	627		

* Time from Admission of Ethylene

T A B L E 52

FINAL OBSERVED ACTIVITIES OBTAINED FOR PALLADIUM

A	ETHYLENE HYDROGENATION
B	ETHYLENE EXCHANGE
C	EVACUATION
D	ADMISSION OF HYDROGEN ALONE

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	663	493	170	65
B	631	440	191	73
C	197	39	158	60
D	184	39	145	55

* Saturation Activity Corrected for Dead Time 263 c. p. m.

Saturation Pressure 5.9×10^{-2} mm.

4. 21. Summary of Retention Results

The results of the confirmatory experiments are in good agreement with the initial ones with the exception of iridium, section 4. 9. However the new result of section 4. 18. has been confirmed by that of section 4. 19. Two sets are given for each metal in table 53 for ease of comparison.

The increasing order of retention is seen to be:

$Pt < Ir < Rh = Ni < Pd$.

The A, B, C, D nomenclature is maintained in this table. Although retention percentages vary in many cases from A to B etc. for the one metal these variations are not claimed to be significant.

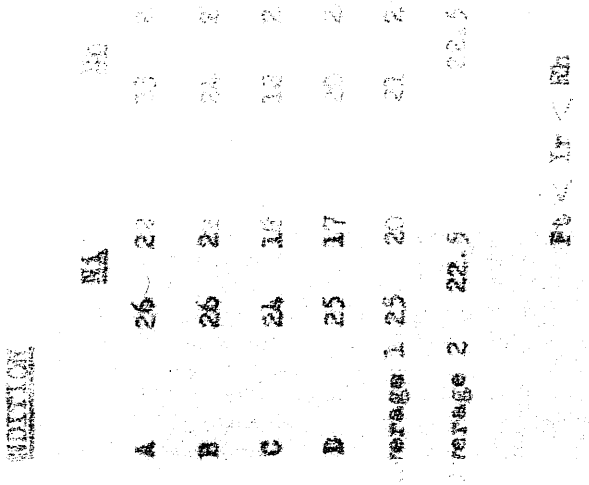


TABLE 53

SUMMARY OF RETENTION FIGURES

Figures Corrected for Dead Time

CONDITION	RETENTION									
	Ni		Rh		Pd		Ir		Pt	
A	26	22	23	21	70	65	13	22	6	7
B	26	22	24	27	72	73	12	17	11	9
C	24	18	18	24	63	60	8	8	8	6
D	25	17	20	24	63	55	7	17	3	6
Average 1	25	20	21	24	67	63	10	16	7	7
Average 2	22.5		22.5		65		14		7	

$Pt < Ir < Rh = Ni < Pd$

4. 22 Poisoned Catalysts

The palladium catalyst had, on occasion, been found to give no hydrogenation of ethylene.

It was decided therefore to find the reason for this catalyst poisoning and air was suspected as a possible contaminant. Accordingly a small quantity of air was allowed to enter the reaction vessel and remain in contact with a reduced catalyst for 15 minutes. The air was then pumped off and a complete run carried out. The main aim was to observe if this treatment rendered the catalyst inactive for hydrogenation. However the usual adsorption studies were carried out as well. 120 mg of the palladium catalyst was chosen for this work. 3.59 ml of air at atmospheric pressure was allowed to enter the reaction vessel from a calibrated pipette. This gave a pressure of 3.1 mm in the reaction vessel.

4. 23. Results on Poisoned Palladium Catalyst

T A B L E 54

ADSORPTION ISOTHERM

120 mg 5% PALLADIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
210	72	138
277	126	151
346	140	206
401	162	239
424	191	233

T A B L E 55

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

120 mg 5% PALLADIUM ON ALUMINA

NO REACTION

TIME	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	349	18	312
2	316	20	322
4	291	22	309
6	326	24	313
8	315	26	321
10	290	28	318
12	297	30	312
14	316	32	324
16	290		

T A B L E 56

FINAL OBSERVED ACTIVITIES OBTAINED FOR PALLADIUM

A ETHYLENE-HYDROGEN EQUILIBRIUM

B EVACUATION

C ADMISSION OF HYDROGEN ALONE

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	318	212	106	45
B	132	31	101	43
C	137	31	106	45

* Saturation Activity Corrected for Dead Time 237 c. p. m.

Saturation Pressure 1.8×10^{-2} mm.

4. 24. Repeat of experiment on poisoned palladium catalyst.

A new catalyst sample was prepared in the usual way and the previous experiment repeated.

T A B L E 57

ADSORPTION ISOTHERM

115 mg PALLADIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
593	279	314
1050	483	567
1229	588	641
1515	842	673

TABLE 58

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

115 mg 5% PALLADIUM ON ALUMINA

NO REACTION

TIME	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	1491	18	1510
2	1516	20	1566
4	1566	22	1532
6	1561	24	1567
8	1581	26	1468
10	1491	28	1521
12	1490	30	1522
14	1530	32	1528
16	1498		

T A B L E 59

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

115 mg 5% PALLADIUM ON ALUMINA

ETHYLENE PRESSURE 6.0 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	1022	18	1025
2	1031	20	1074
4	1048	22	1015
6	1030	24	1054
8	1000	26	1020
10	1006	28	1057
12	1015	30	1048
14	1072	32	1013
16	1056		

* Time from Admission of Ethylene

T A B L E 60

FINAL OBSERVED ACTIVITIES OBTAINED FOR PALLADIUM

A ETHYLENE-HYDROGEN EQUILIBRIUM

B ETHYLENE EQUILIBRIUM

C ADMISSION OF HYDROGEN ALONE

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	1521	873	647	99
B	1030	353	677	103
C	719	40	679	103
D	698	40	658	100

* Saturation Activity Corrected for Dead-Time 668 c. p. m.

Saturation Pressure 6.6×10^{-2} mm.

4. 25. Further experiment on poisoned palladium catalyst

The previous experiment was repeated on the same catalyst without further reduction.

This resulted in the same retention percentage. However during the initial adsorption, although gas phase count rate and saturation pressures were comparable, the surface count was much higher.

In this case the surface count can be compared with the previous result since the same catalyst sample was used again thus maintaining constant geometry.

T A B L E 61

ADSORPTION ISOTHERM

115 mg PALLADIUM ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
1393	262	1121
1852	415	1437
2170	552	1618
2424	750	1674

T A B L E 62

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

115 mg 5% PALLADIUM ON ALUMINA

ETHYLENE PRESSURE

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	2492	14	2465
2	2412	16	2461
4	2470	18	2512
6	2535	20	2455
8	2484	22	2420
10	2430	24	2357
12	2418	26	2477

* Time from Admission of Ethylene

T A B L E 63

FINAL OBSERVED ACTIVITIES OBTAINED FOR PALLADIUM

A	ETHYLENE EQUILIBRIUM
B	EVACUATION
C	ADMISSION OF HYDROGEN ALONE

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	2442	758	1684	102
B	1765	62	1703	102
C	1808	65	1743	103

* Saturation Activity corrected for dead-time 1687 c. p. m.

Saturation Pressure 6.3×10^{-2} mm.

4. 26. Summary of poisoned catalyst results

The reason for doing these experiments was to see if air, could poison the catalyst for hydrogenation. This turned out to be the case.

However the incidental observations made showing a retention of only 44% as compared with 66% in the non-poisoned case suggested that a repeat experiment would be interesting. The repeat experiment gave a retention of 101%. On repeating these observations a result of 102% was obtained. However in this case the saturated surface activity was of the order of 1600 c.p.m. as compared with 650 c. p. m. in the previous case.

It is concluded that while the initial goal in these experiments was achieved an understanding of the other results obtained would require a more protracted study than can be carried out here.

4. 27. The effect of hydrogen pretreatment

It has been observed in the case of evaporated metal films that the order of admission of the reactants is important. The reaction rate is reduced if the catalyst is first treated with ethylene before the ethylene hydrogen mixture is added.

So far our method of study in the case of supported

catalysts has necessarily involved this pretreatment with ethylene. It was of interest therefore to admit a sample of hydrogen to a catalyst before saturating it with ethylene - C -14 in the usual way.

The method adopted was the following: After preparing a nickel catalyst in the usual way hydrogen was admitted to a pressure of 4.5 cm and allowed to remain in contact with the catalyst for 15 minutes before being pumped off. Adsorption studies were then carried out in the usual way. The results are shown in the following tables.

T A B L E 64

ADSORPTION ISOTHERM

329 mg 5% NICKEL ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
732	133	599
1161	183	978
1466	205	1261
2035	300	1735
2714	370	2344
3089	420	2669
3485	535	2950
3660	633	2927

T A B L E 65

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION

329 mg 5% NICKEL ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	2336	45.5 - 36.6 = 9.9
2	2061	
4	1927	
6	1874	
8	1821	
10	1698	45.4 - 35.7 = 9.7
12	1737	
14	1646	
16	1722	
18	1685	
20	1646	45.3 - 35.8 = 9.5
22	1602	
24	1595	
26	1646	
28	1668	
30	1595	45.2 - 35.9 = 9.3
32	1610	

4. 28. Results for hydrogen pretreated catalyst.

T A B L E 66

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

329 mg 5% NICKEL ON ALUMINA

ETHYLENE PRESSURE 4.4 cm

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
min.	c. p. m.	min.	c. p. m.
0	1319	18	1244
2	1315	20	1243
4	1212	22	1271
6	1263	24	1253
8	1279	26	1238
10	1322	28	1192
12	1215	30	1274
14	1246	32	1266
16	1280		

* Time from admission of ethylene.

T A B L E 67

FINAL OBSERVED ACTIVITIES OBTAINED FOR NICKEL

A	ETHYLENE HYDROGENATION
B	ETHYLENE EXCHANGE
C	ADMISSION OF HYDROGEN ALONE
D	EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
A	1618	911	707	23
B	1245	484	761	25
C	812	50	762	25
D	791	50	741	24

* Saturation Activity Corrected for Dead-Time 3097 c. p. m.

Saturation Pressure 3.9×10^{-2} mm.

4. 29 Conclusion for hydrogen pretreatment experiment

From the above table it appears that pretreatment with hydrogen made no change in the final result. A retention of 24% was observed.

4. 30. Study of equilibrium between gas phase and adsorbed species

In order to investigate this point a nickel catalyst was prepared in the usual way for adsorption studies. The adsorption isotherm data is given in table 68. The reaction vessel was subsequently evacuated and total count rates observed with time until constancy was attained. The results are given in table 69. The percentage of the initial activity which could not be removed by pumping was 32%, table 71.

Since this retention is greater than that obtained for molecular exchange a quantity of non-radioactive ethylene was admitted to the system. This had the result of reducing the retention figures to 25%. The results are shown in tables 70 and 71.

T A B L E 68

ADSORPTION ISOTHERM

336 mg 5% NICKEL ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
578	101	477
965	139	827
1154	185	969
1548	209	1349
1621	235	1386

T A B L E 69

CHANGE IN OBSERVED TOTAL ACTIVITY DURING EVACUATION

336 mg 5% NICKEL ON ALUMINA

TIME *	TOTAL ACTIVITY	TIME *	TOTAL ACTIVITY
0	1003	22	514
2	894	24	499
4	681	26	503
6	629	28	517
8	597	30	497
10	610	32	521
12	560	34	500
14	540	36	488
16	550	38	510
18	534	40	491
20	568		

* Time from start of evacuation

T A B L E 70

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

336 mg 5% NICKEL ON ALUMINA

ETHYLENE PRESSURE 4.4 cm

TIME *	TOTAL ACTIVITY	TIME	TOTAL ACTIVITY
c. p. m.	c. p. m.	min.	c. p. m.
0	495	18	446
2	483	20	422
4	472	22	444
6	459	24	452
8	464	26	438
10	474	28	440
12	448	30	429
14	457	32	437
16	423		

* Time from admission of ethylene

TABLE 71

FINAL OBSERVED ACTIVITIES FOR NICKEL

A	INITIAL EVACUATION
B	SUBSEQUENT ETHYLENE EXCHANGE
C	FINAL EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c. p. m.	c. p. m.	c. p. m.	%
A	504	61	443	32
B	435	88	347	25
C	417	64	353	25

* Saturation Activity Corrected for Dead Time 1384 c. p. m.

4. 31. Effect of Non-radioactive ethylene pretreatment.

A nickel catalyst was prepared in the usual way. Non-radioactive ethylene was then admitted to a pressure of 2.9×10^{-1} mm and allowed to remain in contact with the catalyst for twenty minutes. The reaction vessel was then evacuated and ethylene - C - 14 admitted to saturate the surface as in the other experiments previously described.

The results of this experiment are given in the following tables.

4. 32. Results for non-radioactive ethylene pre-treated catalyst.

T A B L E 72

ADSORPTION ISOTHERM

315 mg 5% NICKEL ON ALUMINA

OBSERVED ACTIVITIES

TOTAL	GAS PHASE	SURFACE
c. p. m.	c. p. m.	c. p. m.
.574	141	433
1055	165	890
1530	218	1312
2055	251	1804
2392	300	2092
2457	350	2107

T A B L E 73

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR HYDROGENATION.

315 mg 5% NICKEL ON ALUMINA

TIME	TOTAL ACTIVITY	PRESSURE OF REACTANT MIXTURE
min.	c. p. m.	cm
0	1349	44.2 - 37.0 = 7.2
2	1282	
4	1286	
6	1153	
8	1262	
10	1162	44.1 - 37.1 = 7.0
12	1117	
14	1134	
16	1123	
18	1119	
20	1061	44.0 - 37.2 = 6.8
22	1051	
24	1045	
26	1062	
28	1055	
30	1045	43.9 - 37.3 = 6.6
32	1062	

T A B L E 74

CHANGE IN OBSERVED TOTAL ACTIVITY WITH TIME FOR EXCHANGE

315 mg 5% NICKEL ON ALUMINA

ETHYLENE PRESSURE 4.0 cm

TIME * min.	TOTAL ACTIVITY c. p. m.	TIME min.	TOTAL ACTIVITY c. p. m.
0	886	18	766
2	840	20	785
4	832	22	798
6	774	24	740
8	759	26	748
10	771	28	742
12	751	30	736
14	777	32	746
16	771		

* Time from Admission of Ethylene

TABLE 75

FINAL OBSERVED ACTIVITIES FOR NICKEL

A	ETHYLENE HYDROGENATION
B	ETHYLENE EXCHANGE
C	ADMISSION OF HYDROGEN ALONE
D	EVACUATION

CONDITION	TOTAL	GAS PHASE	SURFACE	RETENTION *
symbol	c.p.m.	c.p.m.	c.p.m.	%
A	1046	604	442	21
B	743	285	458	21
C	557	112	445	21
D	527	80	447	21

* Saturation Activity Corrected for Dead Time

4. 33. Discussion of non-radioactive ethylene pre-treatment experiments

If the initially adsorbed ethylene had been retained to the extent of 22.5% as expected, then at most 77.5% would have been removed on evacuation. A subsequent addition of ethylene - C - 14 would then have adsorbed on this vacated fraction of surface or at least have been capable of exchanging with this fraction. This ethylene - C - 14 then ought to have been removed entirely during subsequent reaction. This was not found to be the case. In fact 21% of the ethylene - C - 14 was retained.

This could mean that the initially adsorbed ethylene had been entirely removed from the surface by pumping. Alternatively the second admission of ethylene - C - 14 could have displaced what remained of the first admission from the surface. Neither of these possibilities is acceptable in the light of the foregoing results.

The possibility of the existence of acetylene - C - 14 in the ethylene - C - 14 was then considered. This has been confirmed by The Radiochemical Centre, Amersham, for the particular batch used in this experiment. Acetylene was present to an extent of about 8%.

Acetylene - C - 14 is capable of displacing the initially adsorbed ethylene.

4. 34. Acetylene Contamination.

Ethylene - C - 14 Batch 20, used in this experiment was used also for the confirmatory experiments on rhodium, platinum, iridium and palladium. It has been confirmed by The Radiochemical Centre, Amersham, that no such contamination existed in the batches used in the earlier experiments.

Any acetylene present must be there to an extent of less than 2%, this being the limit of the analytical technique.

It is of interest to consider why the results are in agreement despite the altered composition of the tracer gas during this work. An explanation is suggested in section 4.35 and is further discussed in Chapter 5.

4. 35. Overall conclusion to experiments

The experiments described in this section have shown that the adsorption of ethylene can be measured on catalyst surfaces during reaction.

The extent to which initially adsorbed ethylene is removed from the surface under subsequent hydrogenation conditions has been shown to vary from one catalyst to another. The percentage retention in the case of palladium is 65%. This is much higher than in the other cases and is followed by nickel and rhodium with 22.5% retention. Platinum shows the lowest retention, 7% and between it and nickel and rhodium we have iridium with 14%.

These percentages are closely paralleled in the case of molecular exchange between the adsorbed species and the gas phase. The pre-adsorbed material is again retained to a similar extent.

It has also been shown that this retained material is not decreased by the action of pure hydrogen, nor can it be removed by evacuation.

Poisoning of the palladium catalyst, by the presence of air, has been demonstrated.

In this case, although the catalyst was incapable of promoting hydrogenation, it was still capable of adsorbing ethylene. It appears however that this adsorbed material cannot be removed by exchange either. Two somewhat anomalous results were obtained however in these poison experiments as already noted in section 4. 26. As a result the poison experiments cannot be taken as complete. Nevertheless what has been said would appear to hold.

Two results were obtained which gave a percentage retention of 14% for iridium. However a third result, the one obtained first, section 4. 9 gave 78.5%. It is to be noted however that in this case the hydrogenation rate was slower than for the other two. This indicates a partially poisoned surface.

An experiment was also carried out to observe the effect of pretreatment of the surface with hydrogen. No difference was observed. Nickel was taken as the catalyst for this experiment and gave 24% retention as opposed to 22.5% for the usual procedure.

Subsequently it was shown that the initially adsorbed ethylene is to some extent in equilibrium with gas phase ethylene and consequently may be removed by pumping.

Finally it was shown that acetylene could desorb even the portion of the adsorbed ethylene layer which was retained

throughout the other experiments. Furthermore the acetylene once adsorbed behaved, at least in the presence of hydrogen, in the same manner as ethylene with regard to extent of retention. This suggests that acetylene is hydrogenated to ethylene on catalytic surfaces.

4. 36. Additional Remarks.

It can be seen that the percentage of pre-adsorbed ethylene removed during hydrogenation is the same as that removed during exchange. There is the possibility therefore that hydrogenation is not alone responsible for removal of adsorbed ethylene in the presence of gas phase ethylene. Hydrogenation may be removing only a fraction of the total material desorbed under reaction conditions.

The effect of hydrogen alone would have to be observed in the absence of gas phase ethylene. This however is impossible, if adsorption studies are to be carried out during normal reaction.

It is also useful to be able to follow the overall hydrogenation process by pressure measurements, since this indicates whether the catalyst is active or not. Such measurements have enabled the single high retention observed for iridium, section 4.9 to be accounted for at least partly on the basis of possible oxygen contamination.

Be this as it may however, the object of this work has been

to study adsorption under normal reaction conditions and so the presence of gas phase ethylene is essential.

The iridium case raised the possibility however that what is being measured here is simply the relative case of reduction of the catalyst used. The percentage retentions, if this were true, may be due to residual oxygen, bearing in mind that at least one of these catalysts adsorbs ethylene after having been poisoned with oxygen as recorded in section 4. 23.

However against this view we have the high degree of reproducibility of the results. It is unlikely that a catalyst could be accidentally poisoned to the same extent on two different occasions. Again the conditions of reduction, 500°C for six hours in an atmosphere of hydrogen are likely to have produced effective reduction in the first place.

Eischens and Pliskin noted variation in type of bonding between hydrogen covered and hydrogen free surfaces. After initial treatment of a surface with hydrogen, section 4. 27, no change in the retention figures were observed. This suggests either that the surface cannot be completely outgassed by six hours evacuation at 500°C after the reduction step or that bond type is the same on a hydrogen free or covered surface in disagreement with Eischens and Pliskin.

CHAPTER 5

DISCUSSION

5. 1. Chemical Studies of Adsorption.

The phenomen of self-hydrogenation must be considered in any attempt to interpret the results of this research since the method of study involved pre-adsorption of ethylene.

The adsorption of ethylene on evaporated films of nickel [55,57] palladium[62] and tungsten[98] has been studied. It has been found that initially adsorption proceeds with very small residual pressure. On addition of further quantities of ethylene the gas pressure rises as a result of the production of ethane. Later ethylene also appears in the gas phase. Further adsorption of ethylene takes place until saturation is reached.

These observations have been interpreted in the following way.[55] At low initial coverage, each ethylene molecule dissociates to occupy four adsorption sites, two by dissociated hydrogen atoms and two by the carbon atoms of the ethylene. A double bond is thus maintained in the adsorbed complex. As the concentration of surface complexes gradually increases, a reaction sets in between the adsorbed hydrogen atoms and gaseous ethylene on the adsorbed complex. This process results in a residue of acetylenic complexes on the surface. To explain the kinetics of hydrogenation Beeck[55]

assumed that ethylene was also adsorbed associatively on that part of the surface not covered by the dehydrogenated complexes.

Evidence for dissociative mechanisms was first presented by Sabatier[56] who discovered carbonisation of nickel in the presence of ethylene at 300° C. This may be thought of as a further step in the process described by Beeck.

In agreement with Beeck, Jenkins and Rideal[57] found evidence for acetylenic complexes on evaporated nickel catalysts at 20° C. They also observed that this surface was capable of chemisorbing hydrogen and they arrived at the conclusion that 83.4% of available sites were occupied by acetylenic complexes, while 8.3% were occupied by hydrogen atoms in pairs and a further 8.3% were unoccupied.

These results were compared with the theoretical model of Roberts[58] and of Herington and Rideal.[59]

In this approach a surface of one hundred sites is filled in a random manner until all sets of four contiguous sites are occupied. Pairs of hydrogen atoms are then removed and the sites so vacated, as far as possible, are filled with ethylene which again takes up four sites. When this process is carried to completion the result is 78% sites covered with acetylenic complexes, 13% covered by hydrogen in pairs and the remainder single sites. This is in good

agreement with the experimental results quoted.

It was also shown in this work that the complex covered surface, on being heated to 170°c, gave off hydrogen and that the resulting carbide was soluble giving rise to a clean surface.

It was concluded in this work that associative adsorption does not occur and that ethylene on chemisorption is dissociated to an acetylenic complex and hydrogen, and that no reversible adsorption takes place. A further conclusion was that hydrogenation of adsorbed complexes is of only secondary importance in the hydrogenation reaction. The suggestion is made that hydrogenation may take place between adsorbed hydrogen and gas phase ethylene.

In a second paper Jenkins and Rideal[60] studied the kinetics of hydrogenation on a complex covered and carbided surface and concluded that the hydrogenation did indeed proceed in the manner earlier suggested.

An investigation of ethylene adsorption on iridium has been carried out by Roberts.[61] Ethylene adsorbed rapidly on clean iridium films at 27°C and 100°C yielding methane and ethane as gaseous products. At 27°C a fast initial adsorption was noted, followed by a slower production of ethane and methane. This reaction was temperature dependent and proceeded much more rapidly at 100°C. The relative amounts also depended on the initial dose of ethylene. Apparently a surface saturated with self-hydrogenation residues prevents decomposition to methane.

The hydrocarbon residue was investigated by interaction with deuterium. Apparently only dicarbon fragments were left for the main products were hydrogen deuteride and deuterated ethane

Palladium films have been studied by Stephens [62]. At 0°C ethylene is chemisorbed with very low residual pressure until a coverage of about 70% is reached, after which self-hydrogenation results and continues until the surface is almost covered with acetylenic residues. There are the same number of units of ethane in the gas phase as there are units of ethylene adsorbed.[62, 57] About 80% of the adsorbed hydrocarbon residues can be removed with hydrogen at pressures of less than 5×10^{-2} mm.

These results may be compared with those of Jenkins and Rideal[57] for nickel and with Trapnell[63] for tungsten. In all cases there was initially chemisorption of ethylene with low residual pressure, followed by self hydrogenation and filling of the surface with acetylenic residues. Although these hydrocarbon layers are formed in the same way and have almost identical compositions they have different properties. There is little production of ethane from the surface complexes in nickel whereas 10% of the ethane formed by self hydrogenation on palladium is formed in this way. There is a rapid removal of the major part of the hydrocarbon layer from palladium and rhodium primarily as ethane.

Metal	% Removed	Time	Temp.
Rh	60	1 min	23°C
Pd	50 - 60	5 min	0°C
	70 - 85	24 hr	0°C

These values may be compared with those of Beeck[55] for nickel. At 23°C 20% of the adsorbed residue can be removed in one hour. The products in this case however are 90% saturated polymers, C_4 to C_8 and higher, and 10% ethane. On the other hand Jenkins and Rideal[57] found ethane to be the only product in the case of nickel.

The decomposition of ethylene on nickel has been studied by McKee[65] as a function of temperature in the range - 30°C to 200°C. The catalyst used here was prepared by reduction of nickel carbonyl. Ethylene at a pressure of 6 mm was allowed to stand for four hours over the catalyst at each of the temperatures studied.

At temperatures below 60°C the products were ethane and hydrogen obtained by self-hydrogenation of ethylene. Beeck found no self hydrogenation below - 39°C. However self-hydrogenation was measured down to - 78°C by McKee. In comparison again with Beeck[66] no polymerisation products were obtained at low temperatures. The result may be compared also with that of Morikawa[67] who obtained 29% butane at 0°C. Methane began to appear in the gas phase at

60°C, and at 200°C this consisted of methane only.

The overall composition of adsorbed residues can be calculated in the form of $(C H_n)_x$ [65]. At 0°C n has a value of 1.5. This decreases rapidly with increasing temperature as hydrogen is progressively removed from the surface and reaches a value of 1 at 20°C. These results on removal of hydrogen from the adsorbed layer may be compared with those of Jenkins and Rideal [57] and also with those of Pickering and Eckstrom. [64] The surface became essentially free of hydrogen at 200°C as compared with a temperature of 300°C claimed by Sabatier, [56] for complete carbonisation.

5. 2. Infra-red Studies.

So far we have looked only at the results of chemical methods of studying ethylene adsorption. Recently three reviews have appeared on the use of infra-red [68,69,70] spectroscopy in the study of adsorbed species.

Little, Sheppard and Yates [71] have studied the spectra of adsorbed ethylene on nickel-silica and palladium-silica catalysts. Similar studies of nickel-silica have been carried out by Eischens and Pliskin. [72]

Initial chemisorption of ethylene on palladium led to the appearance of weak bands assignable to olefinic and paraffinic carbon-hydrogen bonds. When ethylene was admitted to hydrogen-covered palladium, ethane immediately appeared in the gas phase. The spectra of the adsorbed species were however the same as those on hydrogen-free palladium.

It was not possible to observe spectra for initially adsorbed ethylene in the case of the nickel surfaces owing to poor transmission in the samples. However on hydrogenation, an absorption spectrum was obtained in the saturated carbon-hydrogen region.

The results obtained here on the hydrogen free and hydrogen covered surfaces of palladium are in disagreement with those obtained by Eischens and Pliskin for supported nickel catalysts. They found less intense olefinic absorption bonds on hydrogen covered nickel

than on hydrogen free nickel.

However both agree that on addition of hydrogen to pre-adsorbed ethylene the olefinic absorption bonds disappear.

Infra-red absorption studies of ethylene adsorption of rhodium mirrors has been reported by Pickering and Eckstrom.[73] It was found that ethane was produced rapidly at room temperature on admitting ethylene to the surface. Evidence was obtained which suggested that the adsorbed material consisted of paired carbon atoms. There was no evidence for carbon-hydrogen bonds in the adsorbed molecules which could be removed from the surface at room temperature by hydrogen at pressures less than 1 mm.

5. 3. Magnetic Studies.

Magnetic susceptibility studies of ethylene adsorption have been undertaken by Selwood[74] on nickel-silica catalysts. At 0°C the number of bonds formed on adsorption per ethylene molecule is identical with the number formed by a hydrogen molecule. This indicates associative adsorption and no significant self hydrogenation was noted. It is pointed out that ethylene pressures were kept below 1 mm to lower the possibility of self hydrogenation.

Studies of room temperatures, 28°C, showed that no appreciable self hydrogenation took place. Under those circumstances it proved possible to remove 54% of the carbon and of that removed one fifth was in the form of methane and four fifths ethane.

Somewhat less than half the ethylene suffered no very serious reaction at the nickel surface. It was concluded that a substantial fraction of the ethylene was adsorbed associatively though dissociative processes were becoming more important at this temperature.

It was further shown that ethylene adsorbed at room temperature may be heated to 100°C without any change in mode of adsorption. However on heating to 180°C there was a large irreversible change consisting of dissociation and perhaps carbon-carbon bond rupture.

5. 4. Conclusions from the observations.

Selwood attempts to reconcile the many varying experimental observations which have been recorded for ethylene adsorption. His own results show associative ethylene adsorption with a moderate fraction of the dissociative form. Hydrogen is adsorbed in more or less normal fashion in spite of the presence of ethylene and the number of sites accesible to ethylene is only one third the number accesible to hydrogen.

This is in disagreement with the observation of many other workers that the presence of a chemisorbed layer of ethylene on nickel inhibits the hydrogen-deuterium[75] exchange reaction.

Eischens and Pliskins[76] have also found extensive fragmentation of ethylene on hydrogen free surfaces.

If one adds to this all the evidence already referred to in this discussion on self hydrogenation and dissociative adsorption on metal films the results are indeed seen to be conflicting.

Selwood points out that the clue to this lies in the effect of temperature. The loss in magnetisation accompanying adsorption is found to be very much greater at 100°C than at 27°C. A steady state is finally reached at 100°C where six bonds are formed to the surface per ethylene molecule adsorbed. This results in a loss in ability to adsorb hydrogen.

Thus we have the situation that, at room temperature, adsorption occurs by two point associative adsorption and in this way it can exert little poisoning effect for deuterium exchange. As the temperature is raised, fragmentation results, giving increased occupation of nickel sites and poisoning becomes marked.

There remains the objection that slight fragmentation occurs at room temperature, according to Selwood, whereas the results of Eischens imply extensive fragmentation. However it must be pointed out that processes occuring at high temperatures must occur, albeit more slowly, at room temperature and so the result may depend to some extent on the length of time required to carry out an experiment and also on the rate at which the ethylene sample is admitted to the catalyst since adsorption may heat the nickel appreciably.

The value of the heat of adsorption of ethylene on catalysts may also be used to help reconcile the conflicting results. It is noted that most of the evidence for dissociative modes of adsorption has come from studies of ethylene adsorption on evaporated nickel films. Beeck[55] suggested that acetylenic complexes reduced the active area films for hydrogenation, reaction occurring only on those regions not covered by these complexes. He gave rates of ethylene hydrogenation at 0 °C after pre-treatment of the metal with ethylene as a percentage of the rate before this treatment. The order is:

T a, 10% W 20% N i 40% P t, R h 95%

However, more recently, Jenkins and Rideal have suggested that the surface is entirely covered by acetylenic complexes and that reaction proceeds through adsorbed hydrogen atoms and gas phase ethylene.

On the other hand we have the evidence for the reactivity of adsorbed ethylene from exchange reaction reported by Horriuti and Polyani,[77] and Twigg and Rideal[75] who favoured associative adsorption. Farkas[78] found evidence for dissociatively adsorbed reactive species. However it has been generally agreed that ethylene adsorbs before reacting and in favour of the view is the fact that the heat of adsorption of ethylene is greater than that of hydrogen.

The high heat of adsorption of ethylene may however in certain

cases cause the adsorbed species to be fragmented in much the same way as adsorption at high temperatures. Now it is generally observed that heats of adsorption on evaporated metal films are higher than on supported metals [79] or bulk metals [80] Therefore the behaviour of evaporated films at room temperature is similar to that of supported metals at high temperature.

Observations which may be due to this effect are the following. Acetylene is irreversibly adsorbed by evaporated metal films [81] but not by supported metals.[82] Again di-ethylether is decomposed by rhodium films with poisonous residues [83] whereas alumina supported rhodium does not act in this way.[84]

Thus we propose that on clean, unsintered evaporated, films the heat of adsorption may be so great that ethylene is adsorbed with such extensive dissociation of the Beeck type that if hydrogenation is to take place at all it must be between gas phase ethylene and adsorbed hydrogen. In less extreme cases the dissociation will be less severe and while this mechanism may still operate the more generally recognised one involving adsorbed ethylene may now take place. The situation may now be rather more like that which is operative on supported metals at room temperature.

Thus we may imagine the various catalysts which may be studied as being represented by sections on a curve of continuously varying heats of adsorption. On some, with high heats of adsorption, dissociative adsorption may be complete at room temperatures. These are evaporated metal films. At the other extreme we may expect associative adsorption on supported metals. Varying proportions of associative and dissociative adsorption may be observed between these two extremes, depending on the nature, the mode of preparation and the physical state of the catalysts considered. Thus we visualise a gradation in the properties of the adsorbing surface in the case of any one catalyst.

5. 5. Comparison with our results.

The supported catalysts studied in this research may therefore be expected to show two modes of adsorption. In fact a fraction of the initially adsorbed ethylene is removable during subsequent hydrogenation and a similar fraction may be molecularly exchanged with gas phase ethylene. Again in the case of the nickel catalyst, the only one thus studied, it was found that two thirds of the initially adsorbed material could be removed by evacuation.

These observations indicate at least two forms of adsorption. Furthermore the fraction retained in the case of hydrogenation and molecular exchange varies from one catalyst to another showing that the two modes of adsorption occur to varying extents on these

catalysts. In comparison with the results of Jenkins and Rideal [57] and Wishlade [45] who find no reversible adsorption on evaporated nickel films it is seen that the overall strength of bonding to supported metals may be less strong. These results are in good general agreement with the conclusions of the previous section. We may suppose that of the two types of bonding one is associative and the other dissociative. It is unlikely, in the light of the foregoing survey, that carbide formation has occurred on these supported metals at room temperature.

It remains now to attempt to decide which of these two types of adsorbed species is reactive and thus removed from the surface, and which is non-reactive and retained.

5. 6. Associative Complex, Reactive.

It is proposed here to consider the associatively bonded complex reactive and the dissociative complex non-reactive and thus responsible for the retained carbon - 14 in our results. This proposition is examined with regard to other results.

That the dissociative form is unreactive is a proposition in agreement with Beeck [55] who claimed that this type of complex was responsible for poisoning catalysts for the hydrogenation of ethylene. When this type of adsorption occurs to a marked degree on evaporated metal films [57] it necessitates a change in the hydrogenation mechanism to one involving gas phase ethylene

and adsorbed hydrogen.

Now on the basis of what has gone before with regard to the differences between evaporated metal films and supported metals it would appear worthwhile to attempt to correlate the occurence of dissociative adsorption with heat of adsorption and the ability of supported metals to cause carbon-hydrogen bond rupture. That is, an attempt will now be made to correlate extents of retention on the different metals studied with these parameters.

5. 7. Heats of Adsorption.

On trying to examine the assumption that high heats of adsorption cause dissociative bonding which being unreactive results in retained carbon-14 residues it was discovered that the heat of adsorption of ethylene was known for only two of the metals studied. The values are 58 K.cals for nickel and 50 K.cals for rhodium.

However Trapnell [85] on considering the values for the adsorption of a variety of molecules on metals has suggested the following general pattern for heats of adsorption viz:

$$Ni > Rh > Pt > Pd.$$

This is in agreement with our results with the exception of palladium.

Thus there appears to be a correlation of the type sought between heat of adsorption and retention, palladium being an exceptional case.

5. 8. Deuterium Exchange.

Since in forming the dissociative adsorbed complex carbon-hydrogen bonds have to be broken, it is necessary to consider the results of deuterium-hydrocarbon exchange studies on the different metals involved in this discussion.

Anderson and Kemball [86] have studied the exchange of ethane and deuterium over evaporated metal films of molybdenum, palladium and platinum. They define a parameter P such that P is the ratio of the chance of an adsorbed ethyl radical dissociating further to the chance of it leaving the surface as deuterated ethane.

It is found that an initial distribution of products calculated on the basis of a P value of 0.25 agrees with the observed distribution in the case of molybdenum whereas a value of 18 is required for the palladium case. Unfortunately agreement between theory and experiment requires two different parameters for platinum. These are 2 and 18 and they are weighted equally. This renders comparison with our results difficult. Nevertheless we may say that platinum causes less carbon-hydrogen bond breaking than palladium.

However the exchange of methane and deuterium has been studied by Kemball [87] on evaporated metal films. The results show that the fully deuterated methane occurs to the greatest degree with nickel and least with palladium and alternatively the mono-deuterated methane has highest occurrence over palladium and lowest over nickel. The overall order of activity in carbon-hydrogen bond rupture is

$$Ni > Rh > Pt > Pd$$

Thus again we have agreement between this series and our results with the exception of palladium.

It is further stated by Gault and Kemball [88] as a result of deuterium hydrocarbon exchange studies that whereas rhodium was poisoned by residue formation at 0 C, palladium was not so poisoned below 100 C.

Again Kemball [80] observes that rhodium catalyses the breaking of carbon-carbon bonds at moderately low temperatures while palladium is a poor catalyst for this process.

Thus we find again the palladium occurs at the lower end of the sequence instead of the top. The ethane exchange studies show palladium to be more efficient for carbon-hydrogen bond breaking than platinum. However nowhere is there evidence to suggest that palladium should come any higher in the sequence than this.

5. 9. Hydrocarbon Cracking

The cracking of hydrocarbons on metal films has been studied by Anderson and Baker.[89] Strict comparison with the present work is not possible for they used saturated hydrocarbons at temperatures around 450-500° C. None the less carbon-carbon bond breaking led to fragmentation of their hydrocarbons and the relative order of metal reactivity was

$$Rh > W > Ni > Pt$$

This is in reasonable agreement with our retention figures.

5. 10. Conclusion.

In the previous sections we have assumed that the retained carbon-14 on the catalyst studied was due to dissociatively adsorbed species. This assumption was examined by comparing the observed retentions with the occurrence of dissociation as determined by other factors and investigations.

It may be concluded that this attempt has met with moderate success. Agreement has been reached between extent of dissociatively retained complexes and ability to promote bond rupture on the one hand and between retention and heat of adsorption, which is thought to cause dissociation, on the other.

However in all cases considered palladium has been out of sequence.

5. 11. The Anomalous Position of Palladium

The de-activation of palladium-alumina catalysts has been studied by Manly and Rice.[90] They refer to loss in activity of platinum catalysts due to crystal growth and suggest that this factor may cause de-activation in the case of palladium. This is especially likely owing to the low Tamman temperature of palladium. Crystal growth of palladium metal particles can occur at temperatures below 400°C and oxygen is an accelerator for this process. It is suggested that the mechanism may be due to palladium oxide being more mobile than the metal itself.

As pointed out earlier, the palladium catalysts used in this work were found to be more subject to poisoning than the others. It was also demonstrated that oxygen was capable of deactivating them. In addition a high retention was found to accompany a slow rate of reaction on one iridium sample. In view of these facts it is not impossible that the repeated high retention results obtained for palladium may be due to oxygen contamination.

5. 12 Associative Complex Unreactive.

The alternative possibility will now be considered i.e. that the retained carbon - 14 is present on the surfaces as an associatively bonded complex and the reactive material is olefinic in nature.

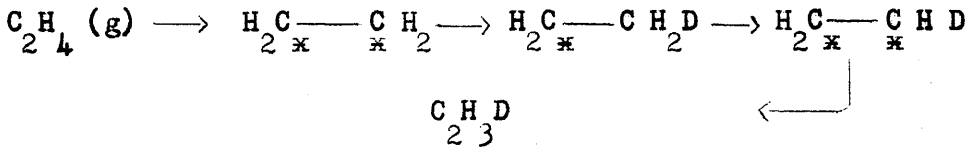
This proposition is in agreement with the infra-red absorption results cited earlier in which olefinic carbon-hydrogen stretching frequencies are seen to be removed on admission of hydrogen to the pre-adsorbed ethylene.[71,72] It is also in agreement with Farkas and co-workers who postulate an olefinic dissociatively adsorbed species as a reactive intermediate.

Previously we have been interested in the ability of a metal to break bonds in adsorbed species, now we are interested in the ability of an adsorbed complex to remain unchanged on the surface. The factor known as alkyl reversal may be expected to provide some evidence on this.

5. 13. Alkyl Reversal

The reactionswhich give evidence on the ability of a catalyst to promote alkyl reversal are olefin exchange[91] and olefin isomerisation.[92]

Olefin exchange is the term given to the following reaction which produces deutero-olefins:



This addition and removal of a hydrogen atoms may give rise, in suitable cases to cis-trans isomerisation or to double bond migration.[99] The order of activity for these processes is

found to be Rh > Pd > Ru > Os > Ir ≒ Pt.

Bond [93] has shown that the above sequence is due to changes in value of a parameter K

where $K = \frac{[C_2H_5]}{[C_2H_4][H]}$

Values of K change to give the sequence

Pt ≒ Ir > Os > Ru > Pd > Rh.

Thus we find that the sequence of activity in olefin exchange and isomerisation is due to the tendency of the metals involved to form associatively adsorbed complexes and that this tendency occurs in the sequence

Rh > Pd > Ru > Os > Ir ≒ Pt.

This compares well with our sequence with the exception of palladium.

5. 14. Comparison with our results

It can be seen that our retention sequence agrees fairly well with the alkyl reversal which is a measure of the tendency of the metals to form associatively bonded ethylene. However it is necessary to distinguish between a high concentration of an associatively bonded reaction intermediate and the retention of associatively bonded complexes.

Nevertheless if we postulate that a proportion of these intermediates become so strongly bonded to the surface, as a result of surface heterogeneity, as to remain adsorbed we have what may be regarded as a correlation.

5. 15. Conclusion

In these last few sections we have been attempting to determine the nature of the retained species observed. The results of this attempt have proved inconclusive.

On taking the view that retention was due to dissociatively adsorbed species of the Beeck type, correlations were obtained with heats of adsorption and bond breaking ability in agreement with the general situation built up in the earlier section with regard to the variations between one catalyst preparation and another.

However on taking the view that retention was due to associatively bonded complexes, which occur extensively on supported catalysts only, another correlation was obtained with the tendency to form associatively bonded species. It may be added that on this view the position of palladium was more in agreement with the retention figures than on the earlier one.

5. 16. Comparison with properties of bulk compounds.

Recently there have been attempts to relate heat of adsorption to heat of formation of corresponding bulk compounds. [94, 95, 96.]

Again attempts have been made to relate stability of complexes with catalytic activity as for example in a recent review of platinum metal salts and complexes as homogeneous catalysts.[97]

With this in mind an attempt was now made to relate stability of olefin-transition metal complexes to the extents of retention on these metals as observed here.

5. 17 General consideration of stability

It is not possible to obtain quantitative information regarding the stability of olefin-transition metal complexes. Values of the required stability constants are not available. An attempt was made however to obtain a qualitative understanding of the complexing ability of the metals with which we are concerned.

To begin with it was necessary to consider, in general terms, the factors likely to influence stability. The bond itself is of the following type.[100] The σ — component is formed by overlap of the vacant anti-bonding Π_z 2 p molecular orbital of the olefin with a vacant 5 d 6 s 6 p^2 orbital in the case of platinum. The Π— component is formed by overlap of the vacant anti-bonding Π_z^* 2 p molecular orbital of the olefin with a filled 5 d 6 s hybrid orbital of the platinum atom.

In the olefin R.Ch = $C H_2$ electron donating groups will strenghten the σ— component and electro-negative substituents will

strengthen the π- component. The stability will depend on the balance of σ- donor and π- acceptor powers of the olefin and on the nature and oxidation state of the metal.[101] It is to be noted that the relative contributions of σ- and π- bonds may vary considerably without altering the strength of the σ-π- bond.

When the hydrocarbon is a non-conjugated poly-oefin e.g. cycloocta - 1, 5 - diene each carbon-carbon double bond interacts separately with the metal atom. In conjugated polyoefins e.g. cyclopentadiene infra-red and nucleur magnetic resonance[102] studies show that it is not possible to decide between separate interaction or interaction with delocalised π- electrons as in ferrocene. Although conjugation favours stability the essential feature appears to be a spatial arrangement of the carbon-carbon double bonds suitable for effective overlap with the metal hybrid orbitals.[103, 104] Mathematical treatment of metal-olefin bonding in terms of molecular orbital theory has been given by Brown[105] and Cotton.[106]

Stable mono-olefin complexes tend to be formed only with metals towards the end of the transition series. Most metals however form stable complexes with diolefins. Fe (o) forms more stable complexes with conjugated diolefins than with chelating diolefins e.g. butadiene

in preference to cycloocta - 1, 5 - diene. The reverse is true of diolefin complexes of Rh (i) and Pd (ii). These differences are illustrated by cycloocta-tetraene which acts as a chelating diolefin in the Rh (i) complex $\left[Rh_2\ Cl_2\ (C_8\ H_8\ )_2\right]$ but as two conjugated diene systems in the complex $\left[(CO)_3\ Fe.\ C_8H_8.\ Fe\ (CO)_3\right]$. The nature and symetry of the metal orbitals determine whether a more stable complex is formed with chelating or conjugated diolefins.[101]

5. 18. Proposals for estimating complexing ability

With this general information in mind it was proposed to estimate complexing ability by considering the following points. First of all does the metal in question form a mono-olefin complex, and if so is the mono-olefin ethylene or does it possess a stabilising group such as propylene? If no mono-olefin complex is formed does it form one with a diolefin and if so is this diolefin conjugated or not? It may be that the metal in question forms none of the above complexes, in which case its ability to form complexes with higher polyolefins will be considered. In all cases ability to form complexes with acetylene will be taken into account.

Although we are primarily concerned with the ability of a metal to complex with ethylene it is necessary to consider other molecules in order to obtain a more general idea of its complexing ability.

5. 19 The Cobalt Group

There are several examples of olefin-cobalt complexes [101] but none appear to involve ethylene. Cyclopentadiene complexes are known however[109] and diolefins such as butadiene and cyclohexa - 1,3 - diene react with di-cobalt octacarbonyl to give

$[Co_2(CO)_6 \text{ di-olefin}]$ $[Co_2(CO)_4 (\text{di-olefin})_2]$

The two bridging carbonyl groups of the octacarbonyl are also replaceable by acetylene to give $[Co_2(CO)_6 \text{ acetylene}]$ [107, 108]

There is no reference to mono-olefin formation in the review by Guy and Shaw.[101]

Rhodium (i) complexes of the type $[Rh_2X_2(\text{diene})_2]$ have been prepared from chelating cyclic diolefins e.g. cyclo-octa - 1, 5 - diene.[110] There is evidence that an unstable complex is formed when rhodium (iii) chloride is treated with ethylene at high pressure.[111] No reference has been found to acetylene complexes of rhodium.[101]

No complex was obtained when iridium (iii) chloride was treated with ethylene[111] or with cyclo-octa - 1, 5 - diene,[110] cf rhodium, but the ethylene complexes $[IrCl_2(C_2H_4)]$ has been reported as formed by the action of ethanol on iridium chloride.[112] Iridium (i) forms stable complexes with cyclopentadiene [113]. No reference has been found to

acetylenic complexes.[101]

Until recently no stable complex of nickel was known. However Schrauzer[114,115] has prepared complexes of the type: $[Ni(un)_2]$ where un = $CH_2{=}{=}CHCN$, $CN.CH{=}CH.CN$, $Ph.CH{=}CH.Cn$ or $CH_2 = CH.CHO$ from nickel carbonyl and the corresponding olefins. Infra-red studies indicate bonding to the carbon-carbon double bonds and not to the nitrate or aldehyde groups.

5. 20 The Nickel Group

Nickel complexes with acetylene[117] are known

$$[Ni_2(C_5H_5)_2(CO)_2] + R.C. \equiv C.R. \longrightarrow [Ni_2(C_5H_5)_2(R.C.\equiv C.R)] + 2\,CO$$

Olefins, u n, react readily with dichloro-bis-benzonitrile palladium (ii) $[PdCl_2(PhCN)_2]$ to form complexes of the type $[Pd_2Cl_4(un)_2]$ which are less stable than the corresponding complexes of platinum.[112]

Recently it has been shown that $[Pd_2Cl_4(C_2H_4)_2]$ may be prepared in benzene solution by the action of ethylene on palladium chloride under pressure.[111]

Chelate complexes of the type $[PdX_2(diene)]$ are readily formed by, for example, hexa - 1, 5 - diene.[116]

Generally the compounds of palladium are more deeply coloured, more easily formed and less stable than their platinum (ii) analogues. No reference to acetylenic complexes was noted.[101]

Most of the early work on olefin complexes was carried out on platinum. This metal forms a variety of complexes among which are $[C_2H_4PtCl_2]$ and of course Zeise's salt $K[PtCl_3(C_2H_4)]$[101]

Platinum acetylenic complexes are also known where the complexing molecule is an acetylenic diol. Methylation of the hydroxyls reduces stability.[118]

5. 21. Summary

From the foregoing survey it is probably possible to draw the conclusion that complexing tendency increases from top to bottom in the periodic table and from left to right.

However to test the generality of this conclusion it was decided to carry out a similar survey of the metals, iron ruthenium and osmium.

5. 22. Iron Group

Olefins readily replace carbonyl groups in the iron carbonyls. However acryonitrile is the only reported example of a mono-olefin complexing with iron. However many poly-olefins are known.[101]

Ruthenium complexes have been reported in the case of ethylene and propylene.[119] These complexes are 1:1 ruthenium : olefin.

Cycloocta - 1, 5 - diene reacts with ruthenium halides to give stable complexes.[120]

Osmuim (iv) does not react with ethylene under pressure[111] or with cycloocta - 1, 5 - diene.[110] However the osmuim (ii) complex $[Os_2 Cl_3 (P E t P h_2)_6] Cl$ gives the stable six co-ordinated complex $[Os Cl_2 (P E t P h_2)_2 (C_8 H_{12})]$ on treatment with cycloocta - 1, 5 - diene which acts as a chelating ligand.[121]

5. 23. Conclusions

In this group it would appear that the greatest complexing power is in the central position at ruthenium. Ruthenium also appears to have greater power than palladium and iron than cobalt. However although this reduces the generality of the conclusions we may still accept them for the cobalt and nickel groups. Thus in those groups complexing ability increases from cobalt to iridium and from nickel to platinum. It was earlier stated that the horizontal trend increased from left to right. However now that the iron group has been included it is seen that ruthenium has greater complexing ability with mono-olefins than either rhodium or palladium, the latter two being rather similar. It may therefore be fair to say that as far as this survey is concerned the tendency in the middle transition series is an increase from right to left.

5. 24. Stability to Hydrogenation

Before considering what bearing these tentative conclusions have on the retention results it is proposed to consider the stability of the bond to the action of hydrogen.

The very stable complex $\left[Fe(CO)_3 (C_4H_6)\right]$ formed by butadiene and iron pentacarbonyl does not react with hydrogen or maleic anhydride indicating the absence of carbon-carbon double bonds.[122, 123] The cycloheptatriene complex $\left[Fe(CO)_3 (cyclo)\right]$ is reduced to the corresponding diene complex by hydrogen using Raney nickel as a catalyst,[124] thus showing that only two of the three carbon-carbon double bonds in the triene are used in bonding to the iron atom.

Cyclo-octatetraene forms complexes with platinum in which only two of the four double bonds are involved in bonding as shown by the uptake of two moles of hydrogen by the complex $\left[Pt\ I_2 (C_8H_8)\right]$.[125] Cycloheptatriene gives the complex $\left[Pt\ Cl_2 (C_7H_8)\right]$ in which two of the three bonds are involved in bonding to the metal.[126]

Thus we see that the resistance to hydrogen of the bond is such that this property is diagnostic for this type of bond.

5. 25. Comparison with our results.

It is seen that the tendency of the noble metals to form

σ-π- bonds and their stability to hydrogenation when formed cannot be related to our retention results.

No relationship exists between the retention results and the position of the metals concerned in the Periodic table. However the tendency to form σ-π-bonded complexes does tend to be periodic.

5. 26. Alternative Approach

So far in this discussion we have attempted to decide which adsorbed species are present on supported metal surfaces at room temperature. Attempts were then made to relate the occurrence of these adsorbed species with the observed retention figures. Later, relationships were sought between retention figures and such metallic parameters as heats of sublimation. Again the idea of σ-π- bonded species was investigated.

It is now proposed as an alternative approach, to take our retention figures and with them try to explain a series of observations so far not considered.

It is observed that the selectivity of the metals studied varies as follows: Pd $>$ Ni $>$ Rh $>$ Pt $>$ Ir.[127]

The sequence of retention figures is: Pd $>$ Ni $\doteq$ Rh $>$ Ir $>$ Pt.

It will be noted that the orders in platinum and iridium do not agree. However this is the only sequence of activities which agree with the retention sequence for palladium with respect to all the others. This question of selectivity will now be discussed

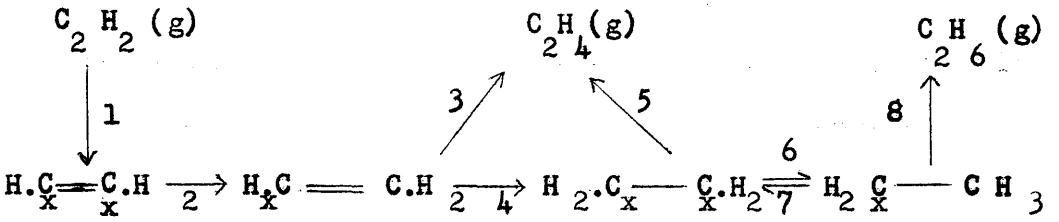
and an attempt made to explain the apparent correlation with retention.

5. 27. Selectivity

All the metals studied in this thesis are catalysts for the hydrogenation of acetylene. The extent to which the olefin is produced as an initial product however varies from metal to metal. Selectivity is defined as the yield of olefin over yield of olefin plus paraffin. It has been established that the paraffin formed in selective hydrogenation is produced during one residence of the hydrocarbon species on the surface.[99] Clearly, further acetylene may be tending to displace adsorbed ethylene formed as an intermediate in the hydrogenation of acetylene to ethane.

However Wells[128] has explained selectivity on the basis of a tendency which the metals show to alkyl reversal. This has been referred to earlier, and is similar to the retention sequence. Palladium is however in the wrong place. However this is not the only factor involved and when the relative activities for hydrogenation of ethylene are considered the sequence of selectivity agrees with that observed and also with our retention figures as referred to in the previous section.

The discussion is carried out by Wells[128] with reference to the following scheme:



Steps 5, 6, 7, 8 are important. The rates of steps 6 and 8 are high on those metals showing high activity in the hydrogenation of ethylene. Step 7 is the alkyl reversal step which acts in opposition to the other two. This step results in a high concentration of associatively adsorbed ethylene and so in an increased loss of ethylene to the gas phase.

5. 28. Proposal

It is now proposed to suggest an alternative explanation of selectivity based on the retention figures obtained in this research and making use of the information already given on the properties of σ-π-complexes.

The problem in selectivity is to explain why adsorbed ethylene produced in the reaction is not hydrogenated to ethane. The retention observations of this thesis show that adsorbed ethylene is not all reactive. Indeed only a fraction of the total can be hydrogenated to ethane and this fraction varies from metal to metal as required to help explain selectivity.

Thus we see that the tendency of the metals to retain adsorbed ethylene is the counterpart of alkyl reversal in the Wells treatment. It is to be observed however that the retention figures tend to support palladium as a greater selectivity catalyst than rhodium whereas alkyl reversal does not.

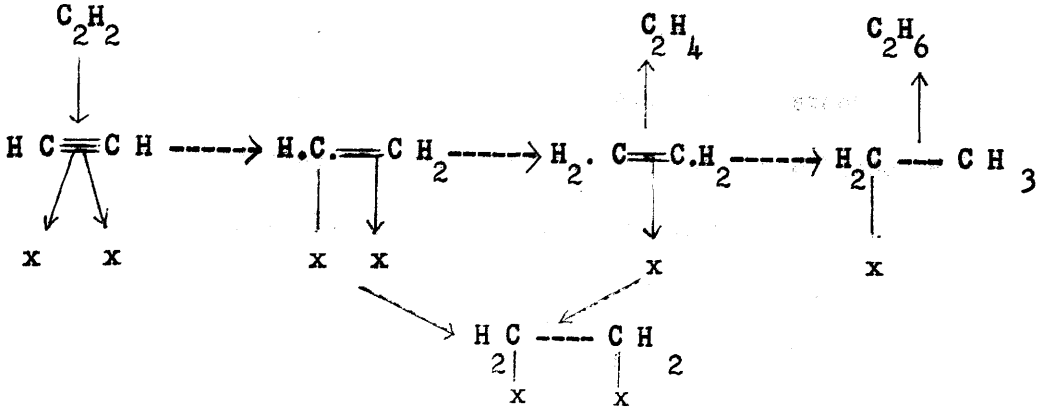
It is only the further consideration of relative activity in ethylene hydrogenation which enables palladium to assume its rightful place in the sequence.

Some figures on selectivity will now be given: [129]

Acetylene	Pd	Ni	Rh	Pt	Ir
Selectivity	0,97	0,83	0.9	0,8	0.2
Temperature °C	30°	80°	132°	97°	24°
But - 2 - yne					
Selectivity	1.00	1.00	0.99	0.96	0.96
Temperature °C	20°-90°	152°	153°	153°	153°

It is to be noted that increase in temperature increases selectivity. Thus it may be seen that palladium is by far the most selective metal. It is also by far the most retentive for adsorbed ethylene.

The proposed reaction scheme is as follows:



Evidence for σ-π-bonded intermediates in catalysis has appeared in the literature.[134] In the above scheme a doubly bonded half hydrogenated acetylene either breaks a carbon σ-bond to form π-bonded ethylene or the double bond is hydrogenated to form associatively adsorbed ethylene. In the absence of acetylene, ethylene adsorbs on the surface as the π-bonded species or the associatively bonded species. The associatively bonded complex is thought to be retained.

In comparing with the Bond-Wells treatment we find that the retention concept offers an explanation of selectivity which gives an order more in agreement with observation than the concept of alkyl reversal and furthermore that it does not involve an adsorbed species which is reducible to ethane.

Thus the second factor in selectivity viz the relative activities in ethylene hydrogenation may be taken separately.

5. 29 Order of Activity in ethylene hydrogenation

We have the observation that σ-π- bonds are resistant to hydrogenation and also the relative strengths of these bonds to the various metals. Suppose that such bonds formed to metal surfaces are uniformly reduced in strength to such an extent that they all become susceptible to hydrogenation. Then those which in the isolated complexes have medium strength may now be expected to have optimum activity for hydrogenation. Thus rhodium and palladium can be understood to be better hydrogenation catalysts than nickel in which interaction between olefin and catalyst may be too weak. They will also be better than iridium and platinum in which cases interaction may be too strong.

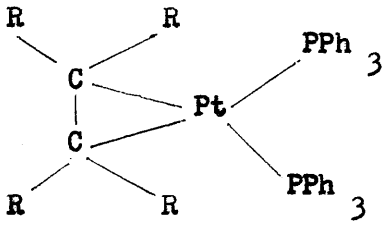
Thus we find that the present scheme accounts not only for selectivity but also for trends in hydrogenation activity.

5. 30. Relationship between σ-π and σ bonds.

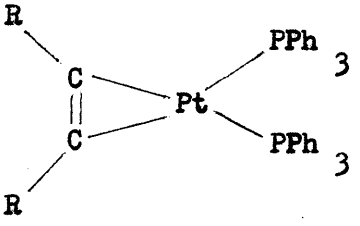
Kharasch [129] in 1936 suggested σ- bonds to explain the existence of the compound bis (ethylene) platinum dichloride. The more satisfactory explanation involving σ-π- bonding resulted from the application of quantum mechanical principles.

However that the difference is more one of degree than kind may

be seen from the following. It is possible [101] that in the stable complexes of the type $[Pt(PPh_3)_2(un)]$ formed by reduction of an alcoholic suspension of cis $[PtCl_2(PPh_3)_2]$ in the presence of an electro-negatively substituted olefin (un) [101] the olefin is bonded to the metal by an essentially pure π — bond although it is equally possible that rehybridisation occurs to two platinum-carbon σ — bonds as shown.



Again complexes of the type $[Pt(PPh_3)_2(ac)]$ have been prepared. [130] Infra-red studies of these compounds indicate that the acetylenic bond has been reduced almost to a double bond and the planer structure



has been postulated.

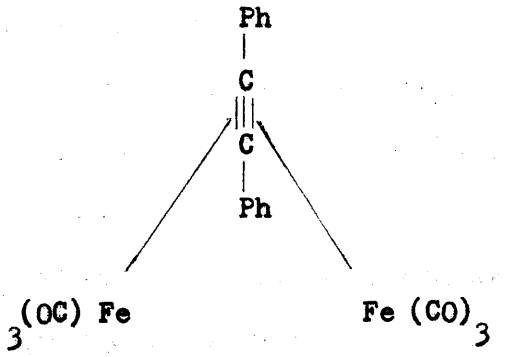
However the transition metals show less tendency to form σ — bonds of the metal-alkyl or metal-aryl type than the other metals. [131]

Indeed platinum is the only transition metal which exhibits this property to any degree.

Thus we can see that both σ-π- and σ- bonds are possible in surface complexes. However there is no real parallel between postulated σ - bonded species in catalysis and similar bonds in stable complexes as there is between the σ-π-bond in these situations.

5. 31. Additional Remarks - 1.

It is suggested in the selectivity scheme that acetylene doubly σ-π-bonds to the surface. Such a system of bonding occurs in the complex resulting from the reaction of diphenylacetylene and iron dodecacarbonyl[101]

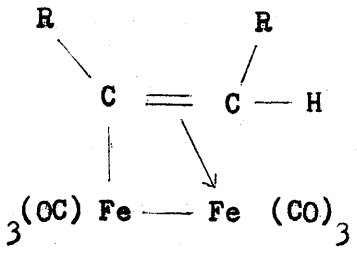


in which some form of double bonding is required between the iron atoms.

- 2.

A complex analogous to the subsequent intermediate in the

proposed selectivity scheme has recently been reported.[132]



- 3.

As a result of the experiment involving pre-treatment of the nickel catalyst with non-radioactive ethylene section 4.32, it was decided that acetylene would displace ethylene from the surface even if present in the non-reactive form. In addition to this the acetylene in the presence of hydrogen then reacts in such a way as to produce this non reactive type of "ethylene adsorption". This is the explanation of the agreement in results whether acetylene is present or not.

These additional results on the behaviour of acetylene are in agreement with the ideas on selectivity which have been dealt with here.

It is perhaps worthwhile to refer to some additional evidence on this point.

Observations by Arthur and Hansen[133] on the adsorption of ethylene in the absence of hydrogen indicate that at about 200°K ethylene decomposes to acetylene (adsorbed) and hydrogen(adsorbed). This

suggests that both acetylene and ethylene are adsorbed in much the same way on surfaces.

Again Little, Sheppard and Yates [71] found similarities between adsorbed acetylene and ethylene on palladium. The surface species derived from initial chemisorption of acetylene on palladium and copper were found to be olefinic in type, as expected. Those from ethylene on palladium were predominantly olefinic but some carbon-hydrogen bonds of saturated groupings could also be detected. Hydrogenation of the surface species gave rise in all cases to stronger spectra of the type found with n - alkyl chains, M. $(CH_2)_n CH_3$; for acetylene on palladium $n > 5$, for ethylene on palladium n - 3.

5. 32.Other possible correlations.

An attempt was made to correlate our retention results with several other metal parameters. This section is best presented as a table.

Parameter	Pd	Ni	Rh	Ir	Pt
Heats of sublimation	93	101	138	165	122
Heats of Formation of oxide	20	58	22	20	29
Work Function	4.99		5.90	5.40	5.27
Melting Point	1552		1960	2443	1769
Lattice Constant	3.8907		3.8031	3.8394	3.9231
Smallest inter-atomic distance	2.751	2.492	2.690	2.714	2.775
% d-bond character	46	40	50	49	44

It will be observed that no correlation exists with any of the above parameters.

5. 33. Conclusion

The conclusion to the experimental results is given in section 4.35. Here we shall deal with what conclusions can be drawn from considering these results in the light of the foregoing discussion.

We can say that the surfaces studied are heterogeneous in that at least two types of bonding, removable and retained, are observed. This probably mirrors an underlying heterogeneity in the surfaces themselves.

The attempt to fit these supported metals into a general scheme involving supported metals and evaporated films has been reasonably successful. In this scheme a gradual variation in 'surface energy' is invisaged graduated from supported metals to non-sintered evaporated films. It is further suggested that any one surface

includes part of this variation and does not simply represent a point on it. Thus we can have two types of adsorbed complex on the one surface although the extents to which they occur vary from one surface to another.

Attempts to decide on the nature of these adsorbed complexes have proved less successful. On the one hand it is possible to correlate the retained activity with the ability of the metal concerned to break molecular bonds, thus indicating that the retained species are dissociated. On the other we have effected a plausible correlation with selectivity data on the basis that the retained activity is due to associatively held complexes.

It is not possible to decide between these two possibilities. However it can be said in favour of the latter that the otherwise anomalous position of palladium may be accounted for. The acetylene experiment is not helpful here since it would appear that acetylene can equally displace ethylene adsorbed on either model.

We have also been able to suggest that acetylene, although it can displace adsorbed ethylene, hydrogenates to adsorbed ethylene on catalyst surfaces and to give an explanation of why this ethylene does not then reduce to ethane with equal ease in all cases.

5. 34. Implications and Future Work.

As suggested in the introduction the demonstration that surfaces are not entirely reactive has implications for attempts to relate activity to bulk properties of the metals concerned, and for calculations of Absolute Reaction Rates.

Although it has been known for some time that surfaces are heterogeneous, different crystal planes showing different rates of reaction, this has not been too important for the above correlations. Since all of the planes were considered active to at least some extent the variation from one to another though presumably 'quantised' was gradual. Thus an overall rate could still be related to some metallic bulk property. However if a considerable fraction of the adsorbing surface is inactive, the chances of effecting such a correlation are somewhat reduced.

Indeed the very heterogeneity demonstrated in this thesis may be the reason why attempted correlations have met with such little success.

It is probable that correlations with bulk properties are only of limited validity in any case. For example the facts of olefin transition metal complex formation may only indicate in a general way the tendency of the transition metals to interact with olefins and so indicate the possibility of catalytic activity.

It is probably more useful to treat catalysts as systems in themselves and to attempt through such techniques as are available to determine the nature of the bonding between metal and substrate. Such similarities and dissimilarities as are uncovered in this way between one metal and another may be discussed in terms of the bonding involved.

So far it has not been possible by the technique adopted in this thesis to decide what type of bonding is involved in retention. It may be possible to go some way towards a decision by carrying out the experiments described here over a range of temperature.

If retention was found to increase with increasing temperatures It would presumably be permissible to ascribe this to carbide formation. However if the associative form of bonding is regarded as occurring to the greater extent at low temperatures and it is responsible for retention, raising the temperature should reduce retention. It may be that retention can be caused by both associative and dissociative adsorption depending on termperature. Indeed both may be present over a certain range of temperature. It would be interesting to try to demonstrate a minimum retention at a certain temperature.

If tritium labelled ethylene could be used in conjunction with carbon - 14 it would be possible to show whether retention was due

to carbide formation since in this case carbon - 14 detection would be expected to indicate carbon residues and tritium could be shown to have desorbed.

Now that this technique has been shown workable the studies referred to in the introduction on variation in support material could be carried out. This provides another parameter with which to gauge the effect of support material.

Without setting down a catalogue of proposed experiments, it is sufficient to say that this technique is capable of further application not only on the present topic, but also in others in the general field of catalysts.

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